10/542280

PC[illegible]U04/00060

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I, JULIE BILLINGSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2003900292 for a patent by IAN JACOBS as filed on 16 January 2003.

WITNESS my hand this
Thirtieth day of January 2004

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Title: Treatment of moulded plastic articles

Abstract: Methods of treatment of moulded plastic articles to improve their stress crack resistance.

Description:

This invention relates to the improvement of ESCR and other properties of flexible injection moulded thin-walled articles by annealing. In particular it relates to the annealing of injection moulded flexible thin walled articles as described in PCT/AU98/00255 and which is hereby incorporated by reference, having a thin section less than 1mm in thickness and wherein the thin section is substantially continuous for greater than 50mm, more preferably greater than 75mm, even more preferably greater than 100mm, yet more preferably greater than 125mm and most preferably greater than 150mm in the direction of flow of the molten polymer blend in the mould. The invention also relates to the annealing of injection moulded flexible thin-walled articles as described in PCT/AU98/00255 made using polymer blends with MFI (defined as I2) greater than 2, preferably greater than 10, more preferably greater than 20, even more preferably greater than 25 and most preferably greater than 30.

Thin-walled tubular containers, such as those used in the cosmetics industry, are currently produced mainly by a combination of extrusion and cutting-to-length of the tube body, injection moulding of the head and shoulders and the welding of said body to said head and shoulders. Low MFI polyethylene (MFI generally less than 2) is the preferred polymer for tube manufacture as it in general imparts the properties of good "feel" and flexibility required by customers and is suitable for extrusion processing. In addition, low MFI low density polyethylene offers sufficient product resistance and barrier properties to make it suitable for most products currently packed into tubes. In cases where the barrier properties of polyethylene are inadequate for particular applications, medium density polyethylene (MDPE), high density polyethylene (HDPE), polypropylene (PP) and multilayer polymer films are commonly used. Because the body of the tube is extruded, low MFI polymers with inherently good ESCR are able to be used in their manufacture. In addition, being a relatively low shear rate process, the extrusion process introduces minimal stresses and molecular orientation of the polymer into the tube body during manufacture. The use of polymers with inherently good ESCR, the relative lack of molecular orientation in extruded and extrusion/blow-moulded tubes as well as the relatively low pressures and processing speeds inherent in the extrusion process results in extruded tubes having low built-in stresses and inherently good ESCR. Consequently, stress relief of extruded tubes by annealing is of minimal value for the vast majority of applications and tube types.

While the injection moulding of flexible thin walled articles such as tubes has been proposed, prior to the developments described in PCT/AU98/00255 it has not been possible to injection mould such articles having relatively long, thin sections without the articles being too susceptible to failure to be of commercial or practical use. The main problems have been associated with the polymers used to injection mould tubes, in that the process of injection moulding a cylindrical or other shaped tube requires the polymer to simultaneously have a high MFI to enable said polymer to flow down the long, narrow and curved path dictated by the tube shape without the use of excessive injection pressures, yet to have sufficiently good mechanical properties to be able to withstand handling and resist the stress cracking effects of many of the products that will be packed in it. To injection mould a tube, requires the

polymer/polymer blend to have flow properties capable of forming moulded parts with radii and a length/thickness ratio of 100 and often much higher. Typically the polymer or polymer blends are required to have MFIs >10, preferably >20, more preferably >30 and frequently >50. It is well known that the physical properties of polymers, particularly ESCR, decrease significantly as the MFI increases, so the inherent ESCR properties of polymer/polymer blends with MFIs required for injection mouded tubes are significantly and inherently lower than those for extruded tubes. To compound this problem forcing a polymer to flow in a mould with such dimensions introduces severe stresses into the polymer, these stresses being "frozen" into the article thus produced when the polymer rapidly cools below its crystallising temperature before these stresses can be relieved. These stresses result in the tube having surprising different and deteriorated properties relative to the other products moulded from the same polymers under less severe moulding conditions.

Further stresses are introduced into injection moulded tubes when they are filled with product and then crimped and sealed - most often by heat sealing or ultrasonic welding. This process involves bending the 'open' end of the tube back on itself through an angle of up to 180^0 to form the fold at the edge of the seal. This fold is in the direction of the flow of the polymer, which direction having been demonstrated to be the direction of maximum weakness of the moulded product. This 'folded and sealed' area, where the tube is required to be deformed in order to effect a seal, is an area of the injection-moulded tube particularly susceptible to stress and flex cracking. Similarly, the body of the tube is permanently distorted – and consequently additionally and permanently stressed – by the crimping/sealing process, as can be readily seen from the distorted shape of the crimped and sealed tube relative to its uncrimped and unsealed shape. These stresses, especially those induced by permanent distortion of the article after crimping and sealing, but also those imposed during the squeezing and flexing of the tube during use, have the effect of significantly reducing the ESCR and other physical properties of the polymers that make up the injection moulded article, thereby making it necessary to use polymers that display unusually good ESCR and other physical properties when moulded into the desired articles. Such polymers/blends may have a number of disadvantages relative to other polymers/blends, such as being more expensive, require longer cooling times (and hence longer cycle times) have greater-than-preferred stiffness (eg. poorer 'feel'), require more intense/expensive compounding, etc.

The following examples illustrate the exceptionally high level of stresses that are moulded into tubes when they are manufactured using the injection moulded process as opposed to the extrusion process. Tubes with 120 X 35mm dimensions were injection moulded using DuPont 2020T polymer, a 1.1 MFI polymer extensively used in commercial extruded tube manufacture and which DuPont describes as "especially suited for injection moulded closure and extruded tubing where flexibility and maximum resistance to environmental stress cracking is required". The injection-moulded tubes were moulded with extreme difficulty, requiring very high injection pressures and temperatures simply to get the 2020T to fill the mould. In each moulding significant degrees of core shifting/flexing were noted, due no doubt to the extremely high injection pressures that were required. In addition, it was noted that the tubes had virtually no resistance to flexing in the direction of the material flow, with significant cracking being induced with less than 5 manual squeezes of the tube. The environmental stress cracking of the same tubes was tested using the ESCR test as herein described, and in spite of claims of "maximum resistance" to environmental stress cracking, was found to be totally inadequate for moulding thin-walled tubes by injection moulding – which is in stark contrast with its status as a 'polymer of choice' for tubes made by the extrusion process. The dramatic degradation of the properties of 2020T when injection

moulded is almost exclusively due to the exceptionally high level of moulded-in and oriented stresses relative to those in tubes extruded from the same material.

In another illustration of the very high level of moulded-in stresses inherent in injection moulded tubes, Dowlex 2517, a 25 MFI LLDPE, was moulded into 150 X 50mm tubes. In a pamphlet on its Dowlex LLDPEs, Dow advises that LLDPEs have substantially better ESCR properties than equivalent high pressure LDPE. To illustrate the difference, a Dow pamphlet states that in one comparative test a high flow Dowlex LLDPE has an ESCR in oil some 80 times better than that achieved by a high pressure LDPE with the similar density and MFI (5700 hrs compared to 70 hrs). It further states that the LLDPE has an ESCR approximately 10 times better than the LDPE when immersed in a 10% Teric solution at 50oC (225 hrs vs 26 hrs). However, contrary to these observations, we have found that when these polymers are moulded in the form of thin walled tubes and ESCR subsequently tested using the ESCR test as herein described, both Dow's 'Dowlex' LLDPE 2517 and Kemcor's LD 8153 (a high pressure LDPE with similar MFI and density) performed poorly in 10% Teric N9 at 50°C, and both failed within 20 minutes, an ESCR that is of the order of 600 times less than that indicated in the pamphlet. The extreme degradation in the ESCR performance of both polymers when injection moulded into tubes is almost exclusively the result of the high level of moulded-in and oriented stresses in the injection moulded tubes.

As an indication of the extent of the increase in strain in the area of a tube that is folded and sealed relative to the unsealed (i.e. open) tube, the strain on the area resulting from sealing was calculated using the formula:

Strain in polymer = Radius of fold/Square of the thickness of the strip.

Assuming a nominal radius for a flat polymer strip of 1 metre and a strip thickness of 0.5mm (a typical wall thickness for a tube), the strain on the unsealed polymer is 0.00025. When sealed, the radius of the strip at the edge of the seal is of the order of 0.65mm, resulting in a calculated strain of 0.385. In other words, sealing the tube results in an increase in strain in the polymer of over 1600 times that in an unsealed tube. For extruded tubes, with their inherently higher ESCR polymer and significantly lower moulded-in processing stresses, this increase in strain presents few problems in terms of ESCR and/or tear strength performance, i.e. annealing articles made using these polymers in combination with the extrusion process is not likely to result in noticeable and/or commercially valuable improvements in ESCR and tear strength of the article. However, in injection moulded thin wall flexible articles, with their significantly higher moulded-in and oriented stresses and intrinsically lower ESCR polymers and hence greater inherent susceptibility to flex and ESCR failure, annealing can make a significant difference to both the ESCR and/or tear strength of the article, and such improvements can make the difference between functionality and non-functionality of the article in terms of its commercial application.

We have now found that annealing a flexible injection moulded thin walled article just before, during or after the article has been filled and/or distorted to its final required shape significantly improves the ESCR and a number of other physical properties of the article, such as resistance to tearing in the direction of the polymer flow when measured using the Gullwing Tear test method (ASTM D-1004). These improvements are most noticeable in the areas of the article that have had additional stresses imposed on them such as occur as a result of any distortion of the article during and subsequent to sealing or having load imposed on it by, for example, stacking. An additional benefit of the annealing of the present invention is that increasing their ESCR etc. enables the use of polymers/blends for the manufacture of

flexible thin-walled articles that would, in their unannealed condition, result in flexible thin walled articles that are either marginal or unsuitable for packaging particular products. During the annealing process the article may, if heated or otherwise treated sufficiently to soften, and/or in cases where the article is sufficiently supported to prevent unwanted distortion of the article, melt the polymer, be reshaped by the application of appropriate forces by various equipment.

While not wishing to be bound by the proposed theory, it is believed that the rapid cooling of the polymer during the injection moulding step from a molten state to below the solidification temperature of the polymer results in various stresses and strains being captured in the solid piece, and that further stresses are introduced as a result of the distortion of the article resulting from the sealing process. These stresses make the article more susceptible to attack by stress crack agents and physical flexing, and hence to failure. This is particularly the case in the period immediately after filling and sealing when, due to the distortion of the moulding resulting from sealing, the stresses within the moulding are at their highest (to an extent, they 'relax' and dissipate over time) and the stress crack agent is in direct contact with the article and can 'attack' the highly stressed areas in the hours subsequent to filling and sealing to cause failure. It is believed that by annealing the polymer, the stresses are quickly relieved before the stress crack agents are able to 'attack' the stressed polymer in order to cause failure. If the stresses are not immediately relieved, it is believed that for many polymer formulations the stress crack agent is able to cause failure of the article before the 'normal' relaxation of the polymer is able to reduce the susceptibility to article failure.

The degree of moulded-in stresses, and hence the degree of reduction in ESCR and other property performance can vary somewhat from moulding to moulding and over time. Thus it is difficult to reliably and accurately compensate for the variation in ESCR reduction between mouldings in the absence of annealing treatment. A further complication is that due to the gradual reduction in stresses over time together with the fact that the extent of stress reduction will depend on the conditions (primarily time and temperature) under which the articles are stored prior to filling and sealing, it is not possible to reliably and consistently forecast how long it may take for all tubes made from a particular polymer formulation to become suitable for use due to natural stress reduction. For this reason amongst others, in order to minimise the possibility of commercial failure due to inadequate ESCR and other property performance, it is currently generally necessary to use polymers with proven exceptionally good ESCR performance when in a stressed state. This limitation has a number of potentially negative aspects, in particular in the areas of potentially higher polymer/unit cost, increased cycle times and less-than-ideal 'feel' and flexibility. It is therefore advantageous if the moulded-in stresses can be relieved before they can substantially adversely affect the commercial performance of the thin walled article.

It has been found that, provided the moulded-in stresses in the injection moulded article are relieved to a greater or lesser extent before the stress crack potential of the product that is filled into the article has sufficient time in contact with the polymer in its stressed state to cause or initiate cracking, flexible thin walled injection moulded articles with improved ESCR and other property performance can be produced. Further, it has been found that annealing the articles enables a much wider range of polymers and polymer blends to be used in the manufacture of commercially useful flexible thin walled articles than is the case if annealing is not practiced.

If there is a significant time lapse between the moulding and filling & sealing operations (eg. if the article is moulded in one location, packed and then shipped to another location for filling and sealing) and it is desired to effect annealing of the moulding prior to the article being shipped – most conveniently, immediately post moulding - many of the benefits of annealing just prior to, during and/or after distortion of the article can still be achieved by annealing post moulding. The benefits of this may not as pronounced as those that can be achieved by annealing after the article has been distorted, but may, depending on the polymer formulation and moulding conditions, nevertheless be worthwhile.

The benefits of annealing post moulding but pre filling are most noticeable in areas of the moulding that are subjected to least additional stresses upon crimping and sealing. These areas are most frequently those that are relatively distant to the 'crimp and seal' area - for example, those areas relatively near the head and shoulders of a tube. We have found that areas of the moulding that are annealed, allowed to cool and then subjected to considerable distortion such as occurs in and around the sealed area during a crimp and seal operation may manifest dramatically deteriorated ESCR performance relative to the same considerably distorted areas in equivalent unannealed mouldings. This is illustrated by the ESCR test as herein described, in which three sets of strips of the polymer blend taken from the same area of the mouldings were subjected to said ESCR test. One set of strips was annealed after stapling, another set was not annealed and the third set of strips was annealed prior to stapling. The ESCR results were as follows:

- Only 4% of strips annealed after stapling failed within 190 hrs
- 25% of the unannealed strips failed within 190 hrs
- Virtually all (94%) of strips annealed before stapling failed within only 3.5 hrs.

As the above results illustrate, annealing tubes when they are in a stressed state significantly improves their ESCR relative to unannealed tubes, whereas annealing tubes in an unstressed state and subsequently stressing them results in dramatically reduced ESCR.

Annealing injection moulded thin walled articles may be facilitated by one or more (i.e. a combination) of a variety of annealing means, including subjecting the polymer of the article to various types of electromagnetic radiation such as far infra-red, infra-red, ultra-violet and microwave radiation, sonic, supersonic and/or ultrasonic energy, electrical energy, electron arc, electron beam, plasma (e.g., corona, glow discharge, etc.), steam, heated gas (eg. hot air), magnetic fields, ionising radiation, lasers, radio frequency and direct contact with heated or vibrating surfaces. Also applicable as an annealing process is in situ warming of the article by inserting into it a fluid medium with a sufficiently high temperature and heat content that it is capable of warming said article to a temperature high enough and for sufficient time to facilitate the annealing of said article by the transfer of heat from the medium to the article itself, said warm medium being inserted before, during or immediately after the distortion (if any) of the article. Due to the thin wall nature of the articles, the temperature of the areas of the articles that come into contact with, or are in relatively close proximity to, the medium may assume a temperature close or equal to that of the medium itself. For example, although the specific area of the tube that will be sealed should preferably not come into direct contact with the medium, once the medium has been introduced into the tube the temperature of the area to be sealed will tend towards that of the medium. Provided such temperature is high enough to initiate annealing, it will result in the partial or complete annealing of said areas of the article, including the area of the tube to be sealed. The temperature of the in situ annealing medium should preferably be greater than 18^{0}C, more preferably greater than 22^{0}C, even more preferably greater than 25^{0}C, yet even more preferably greater than 30^{0}C, even

more and most preferably greater than 35^0C. Additional heat-based annealing processes include immersing the article in, or passing the article through, a bath, oven or other apparatus containing or able to direct at or subject the article to a warming liquid or gas or other annealing agent.

The annealing treatment may, depending on the polymer and the article, be carried out prior to, during or after the distortion of the article. If the annealing process is carried out prior to the distortion of the article, it is beneficial that the effects of the annealing process are still impacting on the polymer during the distortion process. For example, if heat is used to affect annealing and the heat source is removed or significantly reduced prior to distortion of the article, the polymer should preferably still be sufficiently warm during and after the distortion process to enable the annealing of the distorted article to take place. Another method of annealing using heat is to store the final packaged product in heated or naturally warm storage areas, the temperature in which is constantly at or periodically raised or allowed to rise to 22^0C or more, more preferably 25^0C or more, yet more preferably 27^0C or more, even more preferably 30^0C or more and most preferably 35^0C or more for sufficient time to anneal the article or part thereof as measured by an improvement in ESCR (environmental stress crack resistance as measured by the test as herein defined) and/or Gullwing tear resistance in the direction of the flow of the polymer relative to the unannealed article or part thereof.

The entire article doesn't necessarily need to be annealed to achieve the beneficial effects of the invention. If desired, the annealing process can be directed to one or more areas of the article in which it has been determined annealing will have particularly beneficial effects, such as those areas in the injection moulded article that are most susceptible to ESCR or other mechanical failure. Partial annealing of the article may be achieved by, for example, annealing some parts of the article by, for example, infrared radiation while shielding other parts of the article from the radiation. In the case of a tube, areas that may be beneficially selectively annealed include the crimped/sealed and adjacent area and other areas of the tube that are distorted and consequently have additional and unusual stresses imposed on them as a result of the crimping/sealing area processes. In addition, annealing can take place in one or more stages. For example, part of the article may first be subjected to annealing by, for example, filling it with a warm fluid medium. This will anneal mainly those areas of the article that are in contact with and/or close proximity to the warm fluid medium. When the article is a tube, this initial annealing process will primarily anneal the body of the tube, although if the medium is sufficiently warm and sufficient time is allowed, it may also anneal other areas of the tube, such as the area to be crimped and sealed. Subsequent to the initial annealing, and in a separate operation, the tube may then be crimped and sealed at the open end, which will anneal this portion of the tube.

The extent of the desired annealing of a particular article can be determined by experimentation, and may vary depending on the extent/intensity of the deleterious effects of product to be packed into the article on the article as well as the nature of the polymers/blends used to mould the articles and the moulding conditions used in the manufacture of the article and the desired properties of the treated article. Particularly deleterious products (i.e. with high stress cracking potential) may beneficially be packed into articles which have been more extensively annealed that the same article intended for use with a less deleterious product. Similarly, articles that have higher levels of stress due for example to their shape, the conditions of their manufacture and/or the extent of additional stresses imposed on them due to filling, crimping and sealing, etc. may benefit from more intensive annealing than would otherwise be the case.

When increasing the temperature of the article is the annealing method, a wide variety of heating techniques can be used to practice the essential heating step. For example, the articles can be immersed into a hot aqueous bath for sufficient time to heat them to within the desired temperature range. The particular residence time within the hot aqueous bath can depend on a variety of factors such as the shape and/or thickness of the articles and whether the aqueous bath is quiescent or agitated, whether the bath size to number of articles results in fluctuation of bath temperature, and other factors. This annealing method is particularly useful in cases where it is desirable that the filled contents of the article are also heated above a particular temperature, such as in retorting of some foods. The pieces can then be removed from the aqueous bath, dried, and cooled to ambient temperature. In addition to the conduction heating in an aqueous bath, in a preferred embodiment, the heating step is practiced with radiant heating.

In even more preferred embodiments, the radiant heating comprises heating with infrared light. One advantage of radiant heating especially with infrared light is the rapidity with which the heating step can be practiced. Still another advantage is that a separate drying step can be eliminated. Once heated to the desired temperature range, the cooling step can similarly comprise various cooling techniques. Especially preferred for use herein are dry cooling techniques. For example, the articles can be cooled to room temperature with forced air convection cooling. Alternatively, the articles can be allowed to cool naturally, i.e. without accelerated cooling means. The air can be at room temperature or, if desired, can be chilled to shorten the cooling steps duration. In still another variation, ultrasonic heating can be used in substitution for the radiant heating. In still other variations, forced hot air convection heating can be employed. The pieces can be fed into a oven or other heating zones with various combinations of radiant and convection heating.

Annealing is generally defined as the process for removing or diminishing the strains and stresses in thermoplastics. It is often achieved by heating the substance to be annealed and then allowing it to gradually cool. Two successful techniques often employed when annealing thermoplastics include one which withdraws the thermoplastics from a heat source, and the other which causes the heat from the heat source to diminish. Both techniques are often referred to as bulk annealing techniques since they involve heating the interior and exterior of the thermoplastics. The former is generally achieved in lehrs and the latter is generally achieved in ovens. Additional techniques for bulk annealing thermoplastics include those which employ infrared radiation. Thermal annealing is often the preferred method of annealing since simple equipment and techniques are widely and inexpensively available to practice the step. In other, less preferred embodiments, the annealing can be practiced by applying pressure, compression, or tension for a short time.

It is of increasing interest to reduce the stresses and strains of thermoplastics without employing bulk annealing techniques such as the above-described. Accordingly, a process for reducing strains in thermoplastics by surface annealing may be employed which unexpectedly and simultaneously preserves the physical and chemical properties of the thermoplastics. Surface annealing is defined as heating the outer layer of the thermoplastic which is the external layer of the thermoplastic that is often no more than half the thickness of the area to be annealed, for example, 0.25mm thick in the case of a 0.5mm wall-thickness article. Moreover, there is no limitation with respect to the heat source being utilized in this surface annealing other than that it does not cause the outer layer of the thermoplastic and the internal portion of the thermoplastic to be heated to the same temperature, wherein the

internal portion is defined as any part of the thermoplastic not including the outer layer as previously defined. Thus heat may penetrate the internal portion; however, the internal portion is cooler than the outer layer after the outer film layer is surface annealed. Therefore, bulk annealing is prevented. Surface annealing is particularly effective in terms of increasing the ESCR of a thin walled flexible article when the surface that is annealed is the surface that will come into contact with the stress crack agent. The interior wall of a tube or other container, in preference to the exterior wall of a tube or other container, is an example of a surface for which surface annealing is particularly effective. This is because an annealed interior wall of a tube or other container presents the stress crack agent with a surface with reduced stress and hence an improved ESCR relative to an unannealed interior wall, thereby minimising the chances of the stress crack agent being able to initiate stress cracking that could eventually lead to the failure of the tube or container. If the outer surface of the tube or container is the annealed surface, the stress crack agent is able to initiate cracking in the unannealed interior surface with which it is in immediate contact, thereby potentially weakening the tube or container. Annealing of the interior surface of a tube or other container may be achieved by the blowing of hot air onto said surface, the close proximity of a source of radiant heat to the interior surface or other suitable means familiar to those skilled in the art.

When one or more types of electromagnetic radiation is the annealing agent, an article comprised of the polymer should be exposed to the radiation for a time period at least sufficient to absorb enough energy to stress relieve the polymer against stress cracking therein. Exposure occurs at one or more ranges of frequencies which are capable of being absorbed by the polymer and which are effective for stress relieving without or substantially without causing heat induced softening or flowing of the polymer. The electromagnetic radiation is selected from infrared, visible, ultraviolet, microwave, radio, laser and other types of electromagnetic radiation.

It is further noted herein that there is no limitation with respect to the orientation of the thermoplastics to the heat sources employed. Therefore, the heat source and the thermoplastic may be moving, the heat source may move while the thermoplastic remains stationary or vice versa.

Blends of isotactic polypropylene with ethylene propylene copolymers having 4 wt. % to 35 wt. % ethylene, both components having isotactic propylene sequences long enough to crystallize are described in WO 00/01766. Such blends may be suitable for the manufacture of flexible tubes and other containers that are subjected to heating by such methods as heat-filling with the product the container is required to contain and/or heat treating the filled container by methods such as retorting. Blends conforming to the above specification comprise 1% to 95% by weight of the isotactic polypropylene and an ethylene propylene copolymer with greater than 65 percent by weight propylene and preferably greater than 80% by weight propylene. Polymer blends made according to the abovementioned specifications may be suitable for use in the manufacture of flexible tubes and other containers that are subjected to heating by such methods as heat-filling with the product the container is required to contain and/or heat treating the filled container by methods such as retorting.

Blends of various polypropylene polymers and ethylene, propylene or butene α-olefin polymers may be particularly suitable for the manufacture of flexible tubes and other containers that are subjected to heating by such methods as heat-filling with the product the container is required to contain and/or heat treating the filled container by methods such as

retorting. Blends conforming to the above specification comprise component (a) and component (b), with component (a) being at least one isotactic, syndiotactic or atactic polypropylene homopolymer or α-olefin copolymer, preferably one or more of a C2 to C20 α-olefin copolymer, more preferably one or more of a C2 to C8 α-olefin copolymer made with a variety of catalysts such as metallocene or similar catalysts, and component (b) at least one of an ethylene, propylene and/or butene copolymer, preferably a C2 to C20 α-olefin ethylene, propylene or butene copolymer, more preferably a C2 to C8 α-olefin ethylene copolymer made with a variety of catalysts such as metallocene or similar catalysts and featuring a super-random distribution of the copolymer within and amongst the molecular chains of the polymer. The blends consist of 1% to 99% of component (a) and 99% to 1% of component (b), preferably 30% to 99% of component (a) and 70% to 1% of component (b), even more preferably 45% to 99% of component (a) and 55% to 1% of component (b), yet more preferably 55% to 99% of component (a) and 45% to 1% of component (b), and most preferably 60% to 99% of component (a) and 40% to 1% of component (b). Polymer blends made according to the abovementioned specifications may be suitable for use in the manufacture of flexible tubes and other containers that are subjected to heating by such methods as heat-filling with the product the container is required to contain and/or heat treating the filled container by methods such as retorting.

The suitability of a polymer or blend for the application of the present invention, as well as the potential beneficial effects thereof, may be determined by carrying out the ESCR test as herein described, but with the following addition and modifications:

- Prepare two sets of 6 or more strips for subjecting to the ESCR test
- After bending and stapling the two sets of strips, subject one only set of strips to the proposed annealing treatment (eg. an elevated temperature of 50^0C for 30 minutes, allow the strips to cool to 22^0C) and maintained at 22^0C for 2 hrs
- Insert the two sets of strips in the stress crack medium as prescribed by the ESCR test.

The potential benefit of the present invention may be assessed by comparing the ESCR and/or Gullwing tear resistance of the polymer when tested with and without being subjected to the annealing process when in the stressed state. The present invention is particularly applicable and useful for thin walled articles where the difference in time to failure, as measured by the ESCR test as herein described, between annealed and non-annealed strips of the polymer blend used to manufacture the article is >10 hrs, preferably >20 hrs, more preferably > 30 hrs, even more preferably > 50hrs, yet more preferably >100 hrs, even yet more preferably >200hrs and most preferably >350hrs.

Alternatively, the suitability of a polymer or blend for the application of the present invention may be determined by comparing the Gullwing Tear Resistance (measured in the direction of the flow of the polymer) of annealed and unannealed strips cut from mouldings such as may be used in the ESCR test, such strips being of suitable dimensions for carrying out the test. Annealed strips preferably have tear resistance that is more than 5% greater than that of unannealed strips, preferably more than 10% greater, more preferably more than 15% greater and most preferably more than 20% greater. The Tear Resistance of an injection moulded flexible thin walled article is particularly relevant when the article is made of polymers that have a tendency to split or tear relatively easily, such as polypropylene. This tendency to tear or split is often exacerbated when the polymers are moulded into articles that are, by the nature of the moulding process, tool design and moulding conditions, highly orientated. The Gullwing Tear test is particularly useful for assessing the suitability of, amongst other polymers, polypropylene-based polymers and blends thereof (including those cited above) for

the production of injection moulded flexible thin walled articles because such polymers and blends thereof may well pass the ESCR test but still be unsuitable for commercial injection moulded flexible thin walled articles because of poor tear resistance. As is noted above, annealing such articles by means of the present invention may improve their tear resistance to the point where the article develops commercial utility.

The benefit of the present invention is illustrated by the following example. A formulation consisting of 25% Profax SC973 (100 MFI PP ex Basell), 34% Engage 8401 (30 MFI mPE ex Dupont-Dow) and 41% WSG 189 (100 MFI LDPE ex Qenos) was moulded into 165mm long by 0.5mm thick cylindrical tubes under moulding conditions designed to introduce maximum stresses into the moulded tubes. The ESCR of both annealed and non-annealed strips cut from tubes was assessed using the ESCR method described herein. It was found that over 60% of unannealed strips taken from unannealed tubes failed the ESCR test within 2 hrs, whereas no failures were noted in the strips taken from the tubes, said strips having been annealed by heating the stapled strips for 30 minutes at 50^{0}C, cooling to 22^{0}C and conditioning at 22^{0}C for 2 hrs . Further, 94% of the unannealed strips, compared to only 22% of the annealed strips, had failed by 360 hrs. This illustrates that the present invention significantly improves the ESCR of injection moulded flexible thin walled articles, and enables the use of many polymer blends that don't have adequately good ESCR when tested according to the method described herein and which are intended for use for the manufacture of commercially valuable flexible thin walled articles.

The ESCR test for flexible thin-walled articles

As described in PCT/AU98/00255, it has been found that it is possible to injection mould flexible thin-walled articles having relatively long thin-walled sections by selection of the polymers used in the injection moulding process having a time to failure of greater than 10 hours when tested according to the following procedure:

i) a plurality (preferably 6 or more) strips of the polymer blend incorporating any post moulding treatment intended for the final article having the cross-sectional dimensions of 0.65 mm in thickness and 10 mm in width are injection moulded under high shear, long flow length conditions, similar to those intended for use in the manufacture of the flexible thin-walled article.;

ii) the strips are bent back upon themselves and stapled 3 mm from the bend;

iii) the bent strips are immersed in a solution of a stress crack polymer such as an ethoxylated nonylphenol, eg. a 10% solution of Teric N9 (nonylphenol ethoxylated with 9 moles of ethylene oxide - Orica Australia Pty Ltd) and held at a temperature of 50oC;

iv) the strips are observed for signs of cracking, any signs of cracking are regarded as a failure; and

v) the time to failure is when 50% of the strips show signs of cracking.

The ESCR test described above was developed to simulate the stresses that are imposed on the area of the tube that is crimped and sealed after the crimp and seal operation is carried out, this being an area of the crimped and sealed tube that is particularly susceptible to flex and ESCR failure. The need for this special test arose because 'standard' ESCR tests such as ASTM D-1693 are totally inadequate for determining the ESCR of polymers when moulded into flexible thin walled mouldings and subsequently crimped and sealed – a fact clearly illustrated by the comparison between ESCR results on Dupont 2020T and Dowlex 2517 polymers using a 'standard' ESCR and the abovementioned test.

Generally, in order to select a polymer blend suitable for the manufacture of flexible thin-walled articles it is necessary for the polymer blend to have an ESCR as hereinabove defined of greater than 10 hours. Preferably the ESCR of the polymer blend is greater than 100 hours, more preferably greater than 200 hours and most preferably greater than 360 hours. Where the thin-walled article is a tube or other container used for the packaging of a composition such as a moisturiser or a shampoo which may be quite aggressive to the thin walled article and result in a degradation of its properties over time, it is desirable to select a polymer blend having an ESCR sufficiently high such that the thin walled article formed from the blend is able to withstand the rigours of use despite any degradation of properties resulting from the aggressive nature of the materials contained within the thin-walled article. Where the thin-walled article is used for the packaging of a relatively inert material, a lower ESCR may be tolerated.

The ESCR test as hereinabove defined may be conducted using a variety of stress crack polymers. The preferred stress crack polymer is Teric N9 (a 9-mole ethoxylate of nonylphenol ex Orica Australia Pty Ltd), other ethoxylates of nonylphenol may also advantageously be used. Other stress crack polymers may be used and will be selected based upon the desired end-use. Other stress crack polymers include mineral oils, cationic surfactants, solvents and other polymers which will be apparent to those skilled in the art.

Advantageously, the ESCR test as described above is conducted under moulding conditions similar to those to be used in the manufacture of thin walled articles. For example where it is intended to produce the thin walled article using a moulding incorporating melt flow oscillation techniques, it is advantageous to conduct the ESCR tests on panels produced from mouldings made by employing melt flow oscillation techniques. Similarly, the moulding conditions intended for use to mould the thin walled articles, such as injection speed, injection pressure, melt temperature, core and cavity temperature, etc. are advantageously used to produce mouldings for use in the ESCR test.

While the present invention has been described in reference to the illustrated embodiments, it is expected that various modifications in addition to those mentioned above will occur to those skilled in the art, and that methods incorporating such modifications may fall within the scope of this invention, which is defined by the appended claims.

As is noted in PCT/AU98/00255, AU 200020674 A1, AU 72146-99, Australian Innovation Patent No 2002200093 and Australian Innovation Patent 2002100211, all of which are hereby incorporated by reference, the incorporation of at least one compatible agent (an ALOCP) into an at least one polymer (an ALOP) frequently has the effect of substantially improving the ESCR. Such incorporation also frequently improves the Gullwing tear test of the blend. The at least one compatible agent is preferably a polymer and when blended with the at least one polymer results in blends having properties which, when used to mould flexible thin-walled articles such as flexible injection moulded tubes, are superior to the original constituents or the neat polymers. This phenomenon is advantageously used to formulate blends suitable for the injection moulding of flexible thin walled articles .

In a further development relating to the injection moulding of flexible thin-walled articles there are provided polymer blend compositions comprising: (a) an at least one polymer (an ALOP) and (b) an at least one high melt flow compatible polymer (an ALOHMFCP) having an MFI of >100, preferably >200, more preferably >300, even more preferably >500, yet more preferably >1000 and most preferably >1,500. One or more of the polymer components of either or both (a) or (b) may advantageously be produced with a metallocene or similar catalyst system. In the polymer blend, component (a) is preferably about 40 to about 99.9 weight percent of the blend based on the total weight of (a) and (b) and forms the continuous or co-continuous phase of the blend. The polymer blend is formed by mixing blend components (a) and (b) under high shear mixing conditions or other means capable of producing an intimate mix, such as in parallel or series reactors, each reactor producing one or more components of blend components a) and/or b). A unit such as a twin-screw extruder would be an example of a suitable piece of mixing equipment. Other means to achieve a well mixed blend will be apparent to those skilled in the art.

The polymer blend may be prepared by extrusion of some or all of the components of the polymer blend and the resulting chopped extrusion used in the injection moulding process of the present invention. Alternatively, the polymer blend may be provided in its component form and subjected to mixing before and during the melting of the polymer blend in the present process.

An ALOHMFCP is a polymer having an MFI of >100, preferably >200, more preferably >300, even more preferably >500, yet more preferably >1000 and most preferably >1,500. which when blended with the ALOP results in blends having properties which, when used to mould thin-walled articles such as flexible thin wall articles, are superior to the original constituents or the neat polymers. The ALOCP may be selected from the group consisting of ethylene vinyl acetate; ethylene vinyl alcohol; plasticised polyvinyl acetate and polyvinyl alcohol; alkyl carboxyl substituted polyolefins; copolymers of anhydrides of organic acids; epoxy group containing copolymers; chlorinated polyethylene; ethylene-propylene-butylene etc. copolymers; ultra low density, very low density, low density, medium density and high density polyethylene and copolymers thereof; polypropylene, polybutylene and copolymers thereof; polyester ethers; polyether-esters (such as DuPont's Hytrel range); acrylonitrile-methacrylate copolymers; block copolymers having styrene end blocks; half esters; amino and alkoxysilane grafted polyethylenes; vinyl addition polymers; styrene-butadiene block copolymers; acid grafted polyolefins; vinyl pyrrolidine grafted polyolefins; block copolymers of dihydric monomers; propylene graft unsaturated esters; modified polyolefins comprising amide, epoxy, hydroxy or C2 - C6 acyloxy functional groups other polymeric compatibilisers suitable for use with polyolefins; particles coated with any of the above; and mixtures thereof. In the above compatible polymers the functional groups are generally incorporated

into the modified polyolefin as part of an unsaturated monomer which is either copolymerised with an olefin monomer or grafted onto a polyolefin to form the modified polyolefin. Included are ethyl and/or methyl acrylates of ethylene and/or propylene, and ethylene acrylic acid and methacrylic acid copolymer resins.

Also included are blends of compatible polymers, such as a neutralised ionomer such as a Surlyn (Dupont) and EEA and/or EMA and/or EMAA. For example, a low MFI partly neutralised ionomer such as Surlyn 9970 (MFI = 14) may be compounded with a high MFI EMA such as Nucrel 599 (Dupont) (MFI = 500) to achieve a compatible polymer blend with a higher MFI than is achievable with the Surlyn alone, while still being able to benefit from the beneficial properties of the Surlyn. Those skilled in the art will appreciate that the above example is but one of a very wide variety of combinations of compatible polymers that are covered by the present invention.

Alkyl carboxyl substituted polyolefins may include substituted polyolefins where the carboxyl groups are derived from acids, esters, anhydrides and salts thereof. Carboxylic salts include neutralised carboxylic acids and are often referred to as ionomers (eg. Surlyn). Typically acids, anhydrides and esters include methacrylic acid, acrylic acid, ethacrylic acid, glysidyl maleate, 2-hydroxyacrylate, diethyl maleate, maleic anhydride, maleic acid, esters of dicarboxylic acids, etc. Preferred examples include ethylenically unsaturated carboxylic acid copolymers such as polyethylene methacrylic acid and polyethylene acrylic acid and salts thereof. Copolymers of anhydrides of organic acids include copolymers of maleic anhydride as well as copolymers of cyclic anhydrides.

Poly-2-oxazoline compounds and fluoroelastomers are also suited for use as an ALOHMFCP. Incorporation of 1-40%, most preferably 2-20% of poly-2-oxazoline compounds is preferred. These compatible polymers improve the adhesion of the PE blend to various substrates, which may make them useful for printing or labelling. The compatibilizing polymer comprises an α-olefin copolymer substrate grafted with amounts of monovinylidene aromatic polymer. Preferably, the α-olefin copolymer substrate is a terpolymer of ethylene, propylene and a non-conjugated diolefin. Particularly useful as compatible agents and high MFI compatible agents are various aromatic/aliphatic olefin copolymers of which styrene-1,4-butadiene-butylene-styrene bock copolymers (SBBSA copolymers), styrene-butadiene-styrene copolymers (SBS copolymers) and styrene-ethylene-butylene-styrene copolymers (SEBS copolymers) are particularly useful examples for the production of flexible thin walled articles.

Many copolymers of ethylene are also useful as ALOHMFCPs in the process of the present invention. For example single site catalysed polymers such a metallocene catalysed polyethylene and ethylene.

The polymer blends of this invention include, or consist essentially of (a) an ALOP having an MFI of >10, preferably >20, more preferably >30, even more preferably >50, said ALOP being preferably an ethylene or propylene or butene homo or α-olefin interpolymer and preferably produced with a metallocene or similar catalyst which will display narrow composition distribution, meaning that the fractional comonomer content from molecule to molecule will be similar; and (b) an ALOHMFCP, preferably an ethylene, propylene or butene homo or α-olefin interpolymer having a high melt flow rate (i.e. MFI >100) and preferably produced using a metallocene or similar catalyst. All references to metallocene catalysts shall include other catalysts (e.g. single-site and constrained geometry catalysts)

capable of producing polymers having properties the same as or similar to metallocene-produced polymers (e.g. narrow or broad MWD, narrow composition distribution,). Such blends can optionally include additives well known to those skilled in the art, and may include amongst others, additives that reduce the water vapour and/or oxygen transmission rates of the polymers in which they are incorporated. For example, and as described in WO/02/074854 which is incorporated by reference, the addition of between 0.5% and 3% of a low MW hydrogenated aliphatic resin such as poly (dicyclopentadiene) may reduce the normalised moisture vapour transmission and sometimes the O_2 transmission rate of the blend and articles made therefrom.

Polyethylene, as used herein, can be a homopolymer or a copolymer and includes ethylene plastomers, VLDPE, LLDPE, LDPE, and HDPE. Ethylene plastomers, as used herein, refers generally to a class of ethylene based copolymers with density of less than about 0.915 g/cc (down to about 0.865 g/cc). Ethylene plastomers have an ethylene crystallinity between plastics (i.e. linear low density and very low density polyethylenes) and ethylene/α-olefin elastomers. VLDPE is very low density polyethylene, typically having a density in the range of from 0.90 to 0.915 g/cc. LLDPE is linear low density polyethylene, typically having a density in the range of from 0.915 to 0.930 g/cc. LDPE is low density polyethylene, typically having a density in the range of from 0.915 to 0.930 g/cc. HDPE is high density polyethylene, typically having a density in the range of from 0.930 to 0.970 g/cc.

Although PCT/AU98/00255 advises that "a wide variety of polypropylene polymers possessing a very wide range of MFIs (1-200+), densities and crystallinities will produce blends suitable for use in the process of the present invention", it does not describe any particular advantages to be derived from the incorporation of ALOCPs of any nature – including polypropylene polymers – with high (>100) MFIs, and indeed gives no examples of >100 MFI compatible polymers as used in the formulations it describes. In the context of this patent application, a high MFI compatible polymer (an ALOHMFCP) means one or more a compatible polymers, said polymer having an MFI of >100. Note that unless otherwise stated, definitions used in this patent application have the same meaning as the same definition as defined or used in PCT/AU98/00255.

The compatible polymer largely forms the disperse phase of the blends of the present invention. We have now found that, surprisingly, the incorporation of an ALOHMFCP in formulations for the manufacture of a flexible thin walled article frequently has a number of significant advantages relative to the use of the same compatible polymer(s) but with a low (≤100) MFI. We have also found that provided the molecular weight of the ALOHMFCP doesn't fall below a value beyond which its ability to improve the ESCR and/or tear strength in the direction of the polymer flow of the moulded blend is negated, the incorporation of high MFI compatible polymers into the blend has a number of significant advantages relative to the incorporation of low MFI grades of the same compatible polymer. For example, the ALOHMFCP frequently has the effect of increasing the shear sensitivity and overall MFI of the whole blend, thereby improving its flow properties. Also, because there is usually an inverse relationship between MFI and some physical properties of polymers, it is frequently found that polymer properties such as flex modulus and hardness decrease with increasing MFI. When it is desired, for example for reasons of cost, ESCR effectiveness, etc., to use as a particular compatible polymer, but the low MFI grades of that polymer (i.e. polymers with MFIs ≤100) have a flex modulus that is too high relative to the desired application and which results in mouldings and that are too stiff, the substitution of a high MFI chemically similar or identical compatible polymer for all or part of the compatible polymer with an MFI of

≤100 in a blend enables the production and use of blends with much higher MFI than were previously attainable while at the same time reducing the adverse impact on properties such as 'feel' and higher flex modulus that would normally be associated with lower MFI grades of the compatible polymer. Depending on the desired properties of the moulded article, the ALOHMFCP can be used either as the sole compatible polymer in a blend or may be blended with other MFI compatible polymers, which may be either high or low MFI compatible polymers.

Without wishing to be bound by theory, it is believed that the interaction between the ALOP and ALOCP and/or an ALOHMFCP forms regions within the moulded articles which can be regarded as "joints". These "joints" appear to absorb or disperse stresses in articles made from the polymer blend. The presence of these "joints" interspersed within the article appears to absorb or dissipate the stresses within the article which would otherwise result in decreased physical properties. We believe that the benefits obtained from the use of an ALOHMFCP are due primarily to their being more effectively dispersed in the ALOP relative to lower MFI versions of the same compatible agent and that they enable the formation of more and smaller disperse phase particles sizes relative to that attainable with low MFI versions of the same polymer. In general, the higher the MFI of the ALOHMFCP, the smaller the particle size that it can form, although there will be an MFI (and hence MW) beyond which reducing the MW further will not result in further reductions in ALOHMFCP particle size. The smaller particle size of the disperse phase in turn results in an increase of the total surface area of a given weight percentage of the compatible polymer, thereby enabling a greater number of joints and areas of interaction between the ALOP and the disperse phase (i.e. the compatible polymer) of the blend. The effect of reducing the particle size of an ALOCP/ALOHMFCP on the number of particles of the ALOCP/ALOHMFCP in the blend is illustrated by the fact that for a given weight % of an ALOCP/ALOHMFCP in a blend, halving the particle size (eg. by halving the particle radius) of the ALOCP/ALOHMFCP increases the number of ALOCP/ALOHMFCP particles by a factor of 8 and the total surface area of the ALOCP/ALOHMFCP by a factor of 2. Thus halving the radius of the particles of ALOCP/ALOHMFCP increases the number of stress-relieving 'joints' within the moulding by a factor of 8 and the surface area of the interface between the ALOCP/ALOHMFCP and the ALOP by a factor of 2. Both these increases have the potential effect of improving moulding properties such as ESCR and tear strength.

Again without wishing to be bound by theory, we believe that the increase in particle numbers and surface area of the ALOHMFCP of the discontinuous phase is one of the key reasons for many of the property improvements (eg, ESCR, tear strength) of the invention. The improvements in ESCR etc. resulting from the incorporation of high MFI compatible polymers often enables the percentage of compatible polymer in a blend to be reduced while still attaining an acceptable ESCR etc. This may be advantageous, for example where it is desirable to reduce the amount of a PP compatible agent in a blend in order to reduce the flex modulus of said blend. Alternatively, and using the same example, maintaining the weight % of the ALOHMFCP PP results in significant increase in the number of disperse phase particles relative to a low MFI equivalent PP which in turn increases the overall ESCR of the blend. This ESCR improvement in turn enables the use of higher MFI ALOPs, thereby increasing the blend's processing characteristics while maintaining acceptable ESCR performance.

For each type of compatible polymer there will be an upper limit on how high it's MFI (i.e. how low its molecular weight) can be before it starts to unacceptably degrade the

performance of a particular blend for use in a particular application. This upper limit will vary, depending on the characteristics of the particular compatible polymer (e.g. homopolymer or copolymer PP, ionomer etc.), the properties of any other compatible polymers in the blend as well as the characteristics of the ALOP(s) and the interaction between them as well as the end use of the moulded product (eg. what is intended to be packed into the product), and can be determined by experimentation. For some applications some degradation of some characteristics of a particular blend due to the incorporation of one or more high MFI compatible polymers relative to the same blend but with a low MFI version of the same compatible polymer may be acceptable in order to achieve the benefits of the improvement of other properties of the blend that result from their incorporation. Again, the limits on how high the MFI of the ALOHMFCP can be as well as the level of incorporation that can achieved before the blend performance is degraded to an unacceptable level can be determined by experiment.

The ALOHMFCP may be directly produced in a reactor using appropriate catalysts (including metallocenes or similar catalysts) and processing conditions. The ALOHMFCP may also be prepared by 'cracking' lower MFI polymers of the same type by means of various peroxides or other molecular chain-cutting polymers known to those skilled in the art. For example, a 50 MFI polypropylene homopolymer or copolymer may be converted into a high MFI (e.g. a 300, 500, 1,000 or 1500 MFI) polypropylene homopolymer or copolymer by means of cracking it. The cracking required to produce an ALOHMFCP of a particular MFI can be achieved prior to incorporation of the ALOHMFCP into the ALOP, thereby producing a ALOHMFCP ready for incorporation into the blend. Alternatively the ALOHMFCP may be produced in situ in the blend by incorporating into and/or coating the compatible polymer with an appropriate amount and type of a cracking agent capable of cracking the polymer to the required MFI, adding the thus prepared compatible polymer/cracking agent combination to one or more of the other blend components and processing the resultant blend under conditions (usually a high enough temperature) sufficient to enable the cracking agent to reduce the MW (molecular weight) of the compatible polymer to a level that will result in the desired MFI of the compatible polymer. If this latter method of achieving the ALOHMFCP is used, it is necessary to assess the impact, if any, of the cracking agent on the other blend components during processing (i.e. to assess for any unintended cracking or cross-linking of the other blend components by the cracking agent), and if necessary to adjust the blend formulation to correct for the consequences of these effects on the overall properties of the blend. A further method of producing blends of the present invention containing an ALOHMFCP as the disperse phase within a continuous or co-continuous phase of an ALOP is to produce a reactor blend of the ALOHMFCP and ALOP. This may be achieved by a number of means that are well known to those skilled in the art. For example, the ALOHMFCP and ALOP may be produced in a single reactor in the presence of appropriate catalysts. Alternatively they may be produced in parallel or series in two or more reactors, or one polymerized component may be added in its finished state to a reactor in which the other component is being produced.

The ALOHMFCP of the present invention is a compatible polymer or a mixture thereof wherein at least one compatible polymer has an MFI of >100, preferably > 200, more preferably >300, even more preferably >500, yet more preferably >1,000 and most preferably >1500. Unless otherwise stated,. MFI is measured according to ASTM D 1238 (Condition 190°C/2.16 kg). Preferably the high MFI compatible polymer of the present invention is a polypropylene homopolymer, a block or random co or terpolymer of polypropylene, or a mixture thereof, wherein the propylene-based polymer component has an MFI (as measured

by ASTM D 1238 at 230^0C, 2.16kg) of 100 dg/min or more, preferably an MFI of >100, preferably > 200, more preferably >300, even more preferably >500, year to more preferably >1,000 and most preferably >1500. Preferably the propylene-based polymer component copolymer is an isotactic or syndiotactic polypropylene homopolymer or copolymer having a MFI falling within the ranges specified above. Preferably the propylene based polymer will have a MWD of from 1.8 to 4.0 and a narrow composition distribution that is characteristic of metallocene or similar catalysed propylene polymers. However, propylene based polymers such as are cited in US 6,476,173 and which is incorporated by reference and which have MWDs up to 20 will often produce good results. Polymers such as are cited above are conveniently produced using a stereospecific metallocene catalyst system. Random ethylene/propylene/vinyl aromatic interpolymers such as ethylene/propylene/styrene interpolymers may also be used as the compatible and/or ALOHMFCP in the present invention.

A wide variety of polypropylene-based ALOHMFCP, particularly when blended with low molecular weight plastomers, 'substantially linear polyethylenes, metallocene long-chain branched polyethylenes and copolymers of the aforementioned ethylene polymers as the ALOP, will produce blends suitable for use in the process of the present invention. Many monomers have been copolymerized with propylene to form copolymers of propylene for use as compatible polymers . Many high MFI grades of these copolymers are suitable as the ALOP or compatible polymers for use in the present invention.

High MFI polypropylenes suitable as an ALOHMFCP for use in the process of the present invention include isotactic, sydiotactic and atactic polypropylene and blends thereof of various MFIs, densities and crystallinities as would produce desired properties in products moulded by the process of the present invention. Polypropylenes particularly useful as ALOHMFCPs in the present invention are homopolymers or copolymers of propylene and one or more α-olefins selected from ethylene or linear or branched C4 to C20 α- olefins, preferably ethylene or C4 to C8 α-olefins, more preferably ethylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 3,5,5-trimethyl-1-hexene, and 1-octene, even more preferably ethylene or 1-butene or hexene or octene, and optionally, minor amounts of non-conjugated diolefins, preferably C6 -C20 diolefins. In one embodiment, the α-olefin can contain cyclic structures that are fully saturated such that the α-olefin monomer does not contain a cyclic moiety with any olefinic unsaturation or any aromatic structures. Preferred α-olefins are mono-olefins. These propylene copolymers with prescribed range of comonomer levels are preferably prepared by polymerization of the suitable olefins in the presence of supported or unsupported metallocene or similar catalyst systems.

When the propylene-based compatible polymer either consists of or contains one or more copolymers, such copolymers are preferably composed of propylene as a main monomer and an α-olefin other than propylene as the co-monomer. The content of the propylene is generally 70 mole percent or more, more preferably 80 mole percent or more, even more preferably 90% or more and most preferably 98% mole or more. The polypropylene copolymer of the present invention preferably comprises a random crystallisable copolymer having a narrow compositional distribution such as can be produced by metallocene or the like catalysts.

High MFI polyethylene suitable as ALOHMFCPs for use in the process of the present invention may include polyethylenes of various MFIs, densities and crystallinities as would produce desired properties in products moulded by the process of the present invention.

Included are very low, low, medium and high density polyethylene. Particularly when blended with ethylene or propylene α-olefin copolymer low molecular weight plastomers, substantially linear ethylene or propylene α-olefin copolymers or metallocene branched ethylene or propylene α-olefin copolymer, a wide variety of polyethylene polymers possessing a very wide range of MFIs (100-1500+), densities and crystallinities will be ALOHMFCPs suitable for use in the process of the present invention.

High MFI ionomers and chemically related polymers such as EEA, EVA and EMA provide particular advantages as ALOHMFCPs when combined with olefins, particularly ethylene or propylene plastomers, substantially linear polyethylene or polypropylene, and/or branched polyethylenes or polypropylenes as the ALOP. Ionomers are typically copolymers of ethylene and acrylic or methacrylic acids which have been neutralised with metal ions such as sodium, lithium or zinc. One group of ethylene copolymers, called ionomers, are exemplified by the commercial product Surlyn (manufactured by DuPont). Ionomers tend to behave similarly to cross linked polymers at ambient temperature, by being stiff and tough, yet they can be processed at elevated temperatures. Blends of olefins, particularly ethylene or propylene plastomers, substantially linear polyethylenes or polypropylenes, and/or branched polyethylenes or polypropylenes with one or more ionomers are particularly preferred, such blends sometimes providing polymer blends with increased barrier properties and improved optical properties relative to the olefins without the ionomer.

The blend composition of the present invention will generally comprise in the range of about 40 to about 99.9 weight percent of the ALOP which forms the continuous phase or co-continuous phase of the blend when moulded and in the range of about 60 to about 0.1% of a compatible polymer, of which all or part is an ALOHMFCP. These are preferred ranges. The particular ALOP component, the particular compatible polymer component, and the relative amounts of each used in the blend of this invention will depend on the requirements of the particular application for which the blend will be utilized, economics, and other process factors and can be determined by experimentation.

With respect to the physical process of producing the blend, sufficient mixing should take place to assure that a uniform blend, preferably with the ALOCP and/or ALOHMFCP being finely dispersed will be produced prior to conversion into a finished product. Those skilled in the art will be able to determine the appropriate procedure for blending of the polymers to balance the need for intimate mixing of the component ingredients with the desire for process economy. A further method of producing blends of the present invention containing ALOHMFCPs as the disperse phase within a continuous or co-continuous phase of an ALOP is to produce a reactor blend of the ALOHMFCP and ALOP. This may be achieved by a number of means that are well known to those skilled in the art. For example, the compatible and ALOP may be produced in a single reactor in the presence of appropriate catalysts. Alternatively they may be produced in parallel or series in two or more reactors, or one polymerized component may be added in its finished state to a reactor in which the other component is being produced.

Some preferred properties of the final composition when moulded include high tensile strength, flexibility and tear strength. The extractables content for the compositions of the invention and mouldings therefrom is preferably less than or equal to 2.0 wt %, more preferably less than or equal to 1.6 wt %, most preferably less than or equal to 1.4 wt % as measured by ASTM D-5227.

Similar to the function of compatible agents as described in PCT/AU98/00255, the ALOHMFCP of the present invention is used in an amount at least sufficient to improve the environmental stress crack resistance and/or tear resistance, as measured by the Gullwing tear test, of the polymer blend. The high ALOHMFCP may also be used in amounts in excess of those required to compatibilise the polymer blend in order to improve the viscosity characteristics of said polymer blend so as to optimise the moulding characteristics of said polymer blend and/or general properties of the moulded product such as softness and flexibility. Typically, the ALOHMFCP is used in an amount of from about 2 to about 40 weight percent of the polymer blend, although lower amounts may be used in certain polymer blends. The optimum amount for a specific formulation will depend on the properties required and can be determined by experimentation. Further it has been found that inclusion of percentages of ALOHMFCPs that are greater than necessary for increasing the environmental stress crack resistance of the polymer blend will often also enable the improvement of the polymer blend properties such as tear and impact strength, barrier properties, chemical resistance, processing and product feel. For example, the incorporation of greater than necessary percentages of a polypropylene-based ALOHMFCP polymer to improve the environmental stress crack resistance of a polyethylene-based polymer blend to the desired level may improve the chemical resistance and general barrier properties, and reduce the water vapour and water transmission rate of the polymer blend compared to polymer blends containing the minimum amount of polypropylene-based ALOHMFCP required to improve the environmental stress crack resistance only. The properties of such blends of the ALOHMFCP of the present invention may further be modified by the selection of suitable grades of ALOHMFCP and/or the ALOP components to achieve the desired final properties. For example, where it is desired to have a polymer blend containing a relatively high percentage of polypropylene-based polymers, blend properties such as the 'feel', 'softness', impact resistance (especially low-temperature impact resistance), elongation-to-break, tear resistance and/or retortability of such a blend may be substantially modified by utilising a relatively low percentage of low-flex-modulus polymers as the polyethylene-based components of the blend. Examples of suitable low-flex-modulus polyethylene-based polymers include low flex modulus plastomers such as DuPont-Dow Engage 8401 plastomer and some of Mitsui's Tafmer XR propylene/α-olefin copolymers. Further, it has been found that the inclusion of greater than necessary percentages of ALOHMFCP may enable the incorporation of greater percentages of other polymers than would otherwise be consistent with this invention. Thus, using the ALOHMFCP in such quantities may enable the incorporation of greater-than-otherwise-possible amounts of such beneficial, essentially incompatible other polymers such as nylons and EVOH – with concomitant improvements in properties such as tear and impact strength, barrier properties, chemical resistance and product feel.

The ALOHMFCP containing polymer blend may also incorporate a variety of other additives. Examples of additional additives include further polymers, slip agents, anti-tack agents, pigments, dyes, fillers, antioxidants, plasticisers, UV protection, viscosity modifying polymers, additives (some of which may themselves be polymers) capable of reacting with or absorbing deleterious chemicals such as oxygen and other mould release polymers and melt strength modifiers amongst others. Additionally, compatibilisers that improve various properties of the blends – such as weld line strength, compatibility between the ALOP and ALOHMFCP/ALOCP, disperse phase particle size reduction, ESCR, tear strength, etc. – may be added to the blends. The abovementioned and other suitable additives may be added to one or more components of the polymer blend or the polymer blend as a whole prior to moulding in order to modify its properties to suit specific applications or to achieve specific

effects in the end product. In cases where one or more of the additives is itself a polymer, for example in the case of some oxygen-scavenging systems, said polymer may be the ALOP or compatible polymer of the polymer blend. Non-polymer additives may be compatible polymers of the polymer blend.

A wide variety of polymers may be used as the ALOP in blends with an ALOHMFCP of the present invention. These polymers include olefin homopolymers and copolymers, preferably ethylene or propylene or butene homopolymers and copolymers with C3-C20 α or beta olefins and/or polyenes, preferably C3-C8 α or beta olefins, such polymers having densities ranging from very low to high density (density ranges between 0.85 and 0.97 g/cm3). Also suitable for use in the present invention are ethylene, propylene and butene copolymers with terminal vinyl groups and ethylene, propylene and butene copolymers containing greater than 50% ethylene, propylene or butene which are copolymerised with comonomers such as methyl acrylates, ethyl acrylates, acrylic acid, methacrylic acid and other polar comonomers, ionomers, styrene-ethylene/butene-styrene ABA copolymers, styrene, halo- or alkyl substituted styrenes or other vinylidene aromatic monomers and/or one or more hindered aliphatic or cycloaliphatic vinylidene monomers, tetrafluoroethylene, vinylbenzocyclobutane, and naphthenics (e.g., cyclopentene, cyclohexene and cyclooctene). These polymers may be made by a wide variety of methods including high and low pressure processes, using a wide variety of catalysts such as Ziegler-Natta and metallocenes, and have molecular structures ranging from linear to highly branched, thus included are LDPE, MDPE and HDPE. Particularly suitable for use in the present invention are plastomers, 'substantially linear' and branched polyethylenes or polypropylenes, copolymers of propylene and ethylene or one or more α-olefins, terpolymers of ethylene, propylene and one or more α-olefin (of which Montell's Catalloy polymers are an example) and polymers and copolymers of propylene manufactured using metallocene or similar catalysts and which are characterized by a super random distribution of the copolymers. Random propylene copolymers are suitable for the production of flexible thin-walled mouldings, particularly when improved optical clarity is required. Other polymers suitable for use in the present invention include polylactic acid polymers, other suitable biodegradable polymers and polyketones, ethylene carbon monoxide copolymers (ECO), ethylene/propylene carbon monoxide polymers (EPCO), linear alternating ECO copolymers such as those disclosed by U.S. Ser. No. 08/009,198, filed Jan. 22, 1993 and now abandoned, in the names of John G. Hefner and Brian W. S. Kolthammer, entitled "Improved Catalysts For The Preparation of Linear Carbon Monoxide/-Olefin Copolymers," the disclosure of which is incorporated herein by reference, recycled polyethylene (e.g., post consumer recycled high density polyethylene recovered from waste bottles).

As exemplified in JP 07316356, JP 07316355 and JP 07330982 which are incorporated herein by reference, blends of crystalline PP in combination with ethylene/styrene/α-olefin elastomers may be suitable as an ALOP for the production of flexible thin walled articles.

Also suitable for use as ALOPs are linear or branched isotactic polymers, particularly polypropylene and polybutene homopolymers or random copolymers which have a structure in which their tacticity varies within the range of between 25 and 60% of [mmmm] pentad concentration. This variation in tacticity is due to the statistic distribution of stereoscopic errors in the polymer chains. Such polymers are described in, amongst others, WO 01/27169 (P&G), WO/99/52955 (Rieger) and WO 99/52950 and (Rieger) which are hereby incorporated by reference.

Also suitable for use in the present invention are linear or branched isotactic polymers having an arbitary or rather regular sequence of isotactic and atactic blocks within the polymer molecules, such as are described in WO/99/29749 (ExxonMobil), which is hereby incorporated by reference. WO/99/2949 describes a branched polyolefin having crystalline sidechains and an amorphous backbone wherein at least 90 mole percent of the sidechains are isotactic or syndiotactic polypropylene and at least 80 mole percent of the backbone is atactic polypropylene.

Especially when polymers such as are described in the P&G, Rieger and ExxonMobil patents are incorporated in blends having have an MFI >10, preferably >20 more preferably >30 and most preferably >50, and yet more preferably the polymers themselves have an MFI >10, preferably >20 more preferably >30 and most preferably >50, they may be used either as the sole ALOP or as an ALOCP or ALOHMFCP and may have either narrow or broad molecular weight distribution. Polymers such as are described above are often particularly suited to the production of flexible thin walled articles relative to the equivalent polymers of higher tacticity because their relatively reduced tacticity results in polymers with reduced rigidity and increased flexibility and elasticity. If the polymer(s) is used as an ALOCP or ALOHMFCP, it is advantageous – though not necessary - that it is used in conjunction with at ALOP that is made from the same monomer(s) as the ALOCP or ALOHMFCP because this results in greater compatibility/stability between the polymer(s) as well as allowing for easier recycling of injection moulded flexible thin walled articles produced from such blends. For example, if the polymer is a polypropylene homopolymer or copolymer with tacticity varying between 25 and 60% of [mmmm] pentad concentration, it can be blended with a polypropylene homopolymer or copolymer with a higher tacticity to produce a blend suitable for use in flexible thin walled articles. Alternatively, these polymers may be used in conjunction with other polymers to form blends that are suitable for use to manufacture flexible injection moulded thin walled articles. For example, these polymers may be blended with polyethylenes and copolymers of different types, including LDPE, MDPE and HDPE, which in turn may be manufactured using a variety of different manufacturing techniques, catalysts and copolymers such as are described in PCT/AU98/00255 and herein. Preferably, the polyethylene is manufactured using metallocene or similar catalysts.

In many blends suitable for the present invention, it is advantageous to incorporate at least two ALOPs into blends, with at least one ALOP having a higher crystallinity, and preferably a higher MFI, than the at least one other ALOP. It is preferable, though not essential, that the higher crystallinity ALOP (an HCALOP) has a crystallinity that is at least 5% greater, and preferably 10% or more greater than the crystallinity of the at least one other ALOP. The HCALOP may be made by a variety of methods using a variety of catalysts including metallocene, Ziegler Natta, constrained geometry catalysts, or may be produced by a free radical reaction process, and may be linear, substantially linear or branched in structure. In blends in which a HCALOP is incorporated with an at least one lower crystallinity ALOP (which is preferably a metallocene ALOP), better ESCR results are often obtained when the HCALOP polymer has a broad MWD (molecular weight distribution). A broad MWD (i.e. multi modal) HCALOP can be produced by a variety of methods. These include:

1) Intimately blending two or more polymers having different MFIs in appropriate blending equipment;
2) Producing bi or multi modal polymers by means of 'tandem' reactors; and
3) Producing bi or multi modal polymers in a single reactor using appropriate catalysts.

As an example of a multi modal HCALOP, if a formulation for the continuous phase of a blend suitable for the production of flexible thin walled articles calls for a 40 MFI 0.92 density LDPE as the HCALOP in a 30 MFI 0.885 density metallocene ALOP such as Engage 8401, processing and other property improvements may be obtained by substituting the 40 MFI LDPE with a 50:50 blend of a 20 MFI 0.92 and a 60 MFI 0,92 density LDPE. The properties and MFI of the blend of the two HCALOPs in the ALOP can be further varied by varying the ratio between the 20 MFI and 60 MFI, thus enabling a person skilled in the art to vary the properties of the blend according to desire. Relatively minor differences in density between the two HCALOP components are generally not critical to the performance of the blend, so in the above example, the 20 MFI component may have a density of 0.923 and the 60 MFI component a density of 0.919. The acceptability, for a particular end use, of particular density and MFI differences such as are illustrated in the above example can determined by experimentation.

We have found that plastomers, 'substantially linear polyethylenes', metallocene branched polyethylenes and copolymers of the aforementioned ethylene polymers, propylene α-olefin interpolymers and metallocene propylene polymers and interpolymers are preferred ALOPs for use in the present invention for the production of thin-walled products, and especially for the production of flexible thin walled articles. A key characteristic of plastomers, 'substantially linear polyethylenes', metallocene branched polyethylenes and copolymers of the aforementioned ethylene polymers, propylene α-olefin interpolymers and metallocene propylene polymers and interpolymers is their composition distribution ie. the uniformity of distribution of comonomer within and among the molecules of the polymer. Plastomers, 'substantially linear polyethylenes', metallocene branched polyethylenes and copolymers of the aforementioned ethylene polymers, propylene α-olefin interpolymers and metallocene propylene polymers and interpolymers are generally made using catalysts which are known to incorporate comonomer very evenly among and along the polymer molecules they produce. Thus most molecules of a particular plastomer, 'substantially linear polyethylenes', metallocene branched polyethylenes and copolymers of the aforementioned ethylene polymers, propylene α-olefin interpolymers and metallocene propylene polymers and interpolymers will have roughly the same comonomer content, and within each molecule the comonomer will be super-randomly distributed. Another advantage of such catalysts is that the degree of molecular branching within and between the molecules of the polymers produced by them is more uniform than is obtained using conventional catalysts. For example, conventional Ziegler-Natta catalysts generally yield copolymers having a considerably broader composition distribution – and in the case of copolymers the comonomer distribution in polymers thus produced will vary widely among the polymer molecules, and will also be less randomly distributed within a given molecule. Also, the degree of long chain branching is more consistent between molecules produced by metallocene or similar catalysts than are produced by Z-N or similar catalysts.

Plastomers, 'substantially linear polyethylenes', metallocene branched polyethylenes and copolymers of the aforementioned ethylene polymers, propylene α-olefin interpolymers and metallocene propylene polymers and interpolymers are preferred for use in the present invention for the production of thin-walled products, and especially for the production of flexible tubes. These polymers may advantageously have a molecular weight distribution in a ratio Mw/Mn range of 1.5-30, preferably in the range of 1.8-10 and more preferably in the range 2-4. Generally, plastomer, substantially linear or branched ethylene or propylene polymers comprise ethylene or propylene homopolymers and interpolymers of ethylene and/or propylene, with at least one C3-C20 α-olefin copolymer being especially preferred.

The term "interpolymer" is used herein to indicate a copolymer or a ter polymer or the like. That is, at least one other comonomer is copolymerised with ethylene or propylene to make the interpolymer α-olefins. Generally, the α-olefins suitable for copolymerisation with ethylene or propylene to form plastomers contain in the range of about 2 to about 20 carbon atoms, preferably in the range of about 3-16 carbons, most preferably in the range of about 3-8 carbon atoms. Illustrative non-limiting examples of such preferred α olefins are propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, and 1-dodecene and the like. Polyene comonomers suitable for the copolymerisation with ethylene or propylene to form plastomers suitable for the present invention have, in the main, about 3 to 20 carbon atoms, preferably in the range of about 4 to about 20 carbon atoms, most preferably in the range of about 4 to about 15 carbon atoms. In one embodiment the polyene is a diene that has in the range of about 3 to about 20 carbon atoms, and may be a straight chained, branched chained or cyclic hydrocarbon diene. Preferably the diene is a non-conjugated diene. Non-limiting examples of ethylene or propylene/α-olefin co-polymers suitable for the production of flexible thin walled mouldings include ethylene/propylene, propylene/ethylene, ethylene or propylene/butene-1, ethylene or propylene/hexene-1, ethylene or propylene/octene-1, substantially random ethylene/propylene/vinyl aromatic interpolymers such as ethylene/propylene/styrene interpolymers, ethylene or propylene/styrene, halo- or alkyl substituted styrene copolymers. Non-limiting examples of terpolymer plastomers suitable for the present invention include ethylene or propylene/propylene/1,4 hexadiene and ethylene or propylene/octene-1/1,4-hexadiene.

When the ALOP is a plastomer, substantially linear or branched polymer in which propylene or butene constitutes over 50% of the polymer, the MFI of the ALOP α-olefin may be higher than is generally acceptable when ethylene α-olefins constitute the ALOP, due to propylene and butene α-olefins generally possessing better inherent ESCR properties at the same MFI compared to most ethylene α-olefins . Thus many propylene and butene α-olefins, particularly those prepared by metallocene or similar catalysts, can have MFIs up to and greater than 200 and still produce acceptable flexible thin walled articles with good ESCR when used as the ALOP. The optimum MFI for a particular propylene or butene α-olefin ALOP can be determined by experimentation by one skilled in the art, but will preferably be >30, more preferably >50, even more preferably >100 and most preferably >150. α-olefins suitable for copolymerisation with propylene or butene to produce propylene or butene α-olefins suitable for the present invention include α-olefins in the range of about 2 to about 20 carbon atoms, preferably in the range of about 3-16 carbons, most preferably in the range of about 2-8 carbon atoms. Illustrative non-limiting examples of such α-olefins are ethylene, propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, and 1-dodecene and the like. Polyene comonomers suitable for the copolymerisation with propylene or butene to form propylene or butene copolymers suitable for the present invention have, in the main, about 3 to 20 carbon atoms, preferably in the range of about 4 to about 20 carbon atoms, most preferably in the range of about 4 to about 15 carbon atoms. In one embodiment the polyene is a diene that has in the range of about 3 to about 20 carbon atoms, and may be a straight chained, branched chained or cyclic hydrocarbon diene. Preferably the diene is a non-conjugated diene. Non-limiting examples of propylene or butene / -olefin plastomers suitable for the present invention include propylene or butene/butene-1, propylene or butene/hexene-1, propylene or butene/octene-1 and propylene or butene /ethylene copolymers. Non-limiting examples of terpolymer propylene or butene plastomers suitable for the present invention include ethylene/propylene or butene/1,4 hexadiene and propylene or butene/octene-1/1,4-hexadiene. Copolymers of

propylene or butene with other .α.-olefins having 2 to 8 carbon atoms that are particularly useful for the present invention are copolymers comprising propylene or butene and ethylene as indispensable components (monomer units) as well as copolymers of propylene or butene with ethylene and at least one α.-olefin having 4 to 8 carbon atoms usable herein include, for example, 1-butene, 3-methyl-1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, and 1-octene. Further, the copolymer may contain as a comonomer 0.5 to 10% by weight of a nonconjugated diene, such as 1,4-hexadiene, 5-methyl-1,5-hexadiene, 1,4-octadiene, cyclohexadiene, cyclooctadiene, dicyclopentadiene, 5-ethylidene-2-norbornene, 5-butylidene-2-norbornene, or 2-isopropenyl-5-norbornene. Preferably these copolymers are prepared using metallocene or similar catalysts. The percentages of ethylene and/or other α-olefins copolymerised with propylene or butene to form polymers suitable for the present invention can be varied widely, depending on the desired properties of the mouldings made from blends of these materials. In general, the higher the percentage of ethylene and/or α-olefin copolymer polymerised with the propylene or butene, the lower the flex modulus of the resultant polymer and so the more flexible the mouldings made from them will be in which said polymers constitute the ALOP of the blend.

US 6355736, which is hereby incorporated by reference, describes a propylene block copolymer composition comprising (A) a propylene-α-olefin random copolymer with a propylene content of 99.4 to 99.9 mol % and (B) a propylene-α-olefin random copolymer with a propylene content of 35 to 60 mol %. It further describes propylene block copolymer compositions wherein the content of the propylene-α-olefin random copolymer (B) is from 22 to 40% by weight, based on the weight of the propylene block copolymer composition. Such propylene block copolymers are suited for use as ALOPs and/or ALOHMFCPs in the present invention.

US 6458901, which is hereby incorporated by reference, describes propylene copolymers suitable for use as ALOPs and/or ALOHMFCPs suitable for use in the present invention. The propylene copolymers described comprise propylene, at least one olefin selected from the group consisting of olefins having 2 to 20 carbon atoms except propylene, and a cyclic olefin, and are characterized in that the total number of carbon atoms of the monomers except the cyclic olefin is at least 7. The incorporation of cyclic olefins into polymers consisting of propylene, at least one olefin selected from the group consisting of olefins having 2 to 20 carbon atoms except propylene results in the improvement of the heat resistance of the resultant polymer. The propylene copolymer preferably contains 0.01 to 20% by mole, more preferably 0.05 to 15% by mole, particularly preferably 0.1 to 10% by mole, most preferably 0.15 to 5% by mole, of the cyclic olefin. When the propylene copolymer of the present invention comprises ethylene (the olefin having two carbon atoms), the content of ethylene is preferably 80% by mole or less, more preferably 70% by mole or less, particularly preferably 60% by mole or less, most preferably 50% by mole or less, from the viewpoint of the improvement of flexibility of the thermoplastic resin composition.

The SCBDI (short chain branch distribution index) is defined as the weight percent of molecules having a comonomer content within 15% of the median total molar comonomer content. The SCBDI of the propylene polymers suitable for the present invention is preferably greater than about 30%, and especially greater than about 50%, with figures of 70% or more being achieveable.

Without wishing to be bound by theory, we believe that the interfacial tension between two immiscible polymers decreases with decreasing molecular weight, so that as the MFI of the disperse phase increases so does the compatability between the polymers until they become miscible. We further believe that the degradation of the polymer blend properties that may occur if the MFI of the disperse phase is increased above a certain level is due at least in part to the disperse phase becoming miscible in the continuous phase.

Elastic substantially linear, plastomer or branched ethylene or propylene α-olefin polymers can be made with broader molecular weight distributions by means of the appropriate selection of catalysts for the polymerisation process as described in US 5,278,272 and WO/02/074817, both of which are incorporated by reference. Broader MWD material exhibits a higher shear rate or shear stress dependency. In other words, generally the broader the MWD, the higher the effective MFI at high shear, and hence the better the processing characteristics. However, as observed in WO/02/074817, which describes the production of easier processing olefin polymers by producing essentially two or more polymers with roughly the same SCBDI but differing MWs (i.e. producing a high MW copolymer (M_{wH}) and a low MW copolymer (M_{wL}), it has been observed that such polymers with a M_{wH}/M_{wL} greater than 60 may display some deteriorated physical characteristics relative to polymers with M_{wH}/M_{wL} less than 60, and in general, M_{wH}/M_{wL} less than 60 are preferred. The preferred M_{wH}/M_{wL} range is 1.5 to 60, more preferably 1.5 to 40, yet more preferably 1.5 to 15. In some embodiments, the preferred M_{wH}/M_{wL} is between 3 and 15. Broad molecular weight 'substantially linear olefin polymers', plastomers and metallocene branched polyethylenes and polypropylenes characterised by a high I10/I2 MFI ratio particularly suited to the production of tubes by the process of the present invention.

High I_{10}/I_2 polymers suitable for the present invention may be produced by a variety of methods. These include:

1) intimately blending two or more polymers having different molecular weights in appropriate blending equipment;
2) producing bi or multi modal polymers with high I_{10}/I_2 by means of 'tandem' reactors; and
3) producing bi or multi modal polymers with high I_{10}/I_2 in a single reactor using appropriate catalysts.

The catalysts used to produce bi or multi modal polymers with high I_{10}/I_2 may be selected to produce:

1) broad molecular weight distribution polymers (eg. polyethylene copolymers with molecular weight distribution in the 3-30 range such as are described in US patent 5,281,679 which is incorporated herein by reference); or
2) effectively two or more polymers, each having either a narrow or broad molecular weight distribution as desired. US 5,539,076 the disclosures of which are herein incorporated by reference, describes a method of manufacturing bi or multi modal polyethylene polymers with densities between 0.89 and 0.97 in a single reactor.

Examples of blends utilising ALOHMFCP include the following examples. It will be understood that the percentages of the various types of blend components illustrated in these example may be varied depending on the desired properties of the mouldings produced therefrom, and that the range of percentages of the types of blend components that will produce acceptable mouldings may be determined by experimentation. :

Example 1
30% Engage 8401, a 0.885 density, 30 MFI metallocene polyethylene from Dupont Dow
45% WSM 168, a 0.919 density, 63 MFI LDPE from Qenos
25% of Fina 3960, a 350 MFI PP homopolymer from Átofina.

This example illustrates the incorporation of a single ALOHMFCP propylene polymer into a blend of an mPE and an HCALOP LDPE suitable for the manufacture of flexible thin walled articles.

Example 2
45% Engage 8401, a 0.885 density, 30 MFI metallocene polyethylene from Dupont Dow
45% WSM 168, a 0.919 density, 63 MFI LDPE from Qenos
10% of a 1000 MFI PP homopolymer
10% SC973, a 100 MFI PP copolymer from Basell

This example illustrates the incorporation of a combination of ALOHMFCP propylene compatible polymer and a low MFI propylene compatible polymer into an mPE/LDPE blend suitable for the manufacture of flexible thin walled articles.

Example 3
30% Engage 8401, a 0.885 density, 30 MFI metallocene polyethylene from Dupont Dow
15% WSM 168, a 0.919 density, 63 MFI LDPE from Qenos
15% WRM 124, a 0.920 density 22 MFI LDPE from Qenos
40% of a 1500 MFI PP homopolymer

This example illustrates the incorporation of a very high MFI ALOHMFCP propylene polymer into a blend of an mPE, a relatively low (22) MFI LDPE compatible polymer and a relatively high (63) MFI LDPE suitable for the manufacture of flexible thin walled articles.

Example 4
30% Engage 8401, a 0.885 density, 30 MFI metallocene polyethylene from Dupont Dow
30% WSM 168, a 0.919 density, 63 MFI LDPE from Qenos
20% of a 1000 MFI PP homopolymer
20% Catalloy KS-084P, a 30 MFI propylene terpolymer from Basell

This example illustrates the incorporation of an ALOHMFCP propylene polymer in combination with a low MFI, low flex modulus propylene terpolymer into a blend suitable for the manufacture of flexible thin walled articles.

Example 6
30% Engage 8407, a 0.87 density, 30 MFI metallocene polyethylene from Dupont Dow
30% WSM 168, a 0.919 density, 63 MFI LDPE from Qenos
20% of a Nucrel 599, a 500 MFI EMA from Dupont
20% Surlyn 9970, a 14 MFI ionomer from Dupont.

This example illustrates the incorporation of a high MFI non-propylene compatible polymer in combination with a low MFI ionomer into a blend suitable for the manufacture of flexible thin walled articles. In this type of formulation the high MFI non-propylene compatible

polymer is used at least in part to increase the MFI of the low MFI compatible polymer, said low MFI compatible polymer having been found to be particularly useful when utilised in compositions for the manufacture of flexible thin walled articles but which, when used as the sole compatible polymer in a composition, has an MFI that is sufficiently low to significantly reduce the practical utility of the composition.

Example 7

70% propylene/butene copolymer with a butene content of 15%, an MFI of 50 and a MWD of <4 and made by a metallocene/single site catalyst.

30% Exact 4038, a 125 MFI 0.885 density ethylene/butene copolymer from ExxonMobil.

This example illustrates the incorporation of a high MFI mPE compatible polymer into a propylene/α-olefin copolymer ALOP, and which is suitable for the manufacture of thin-walled flexible articles.

Example 8

70% propylene/octene copolymer with an octane content of 20%, an MFI of 30 and a MWD of <4 and made by a metallocene/single site catalyst.

30% of Fina 3960, a 350 MFI PP homopolymer from Atofina.

This example illustrates the incorporation of a high MFI PP compatible polymer into a propylene/octene α-olefin copolymer ALOP, and which is suitable for the manufacture of thin-walled flexible articles.

Example 9

70% propylene/ethylene substantially linear copolymer with an ethylene content of 25%, an MFI of 50 and a MWD of <4 and made by metallocene/single site catalysts.

30% of Fina 3960, a 350 MFI PP homopolymer from Atofina.

This example illustrates the incorporation of a high MFI PP compatible polymer into a substantially linear propylene/ethylene α-olefin copolymer ALOP, and which is suitable for the manufacture of thin-walled flexible articles.

Example 10

80% propylene/butene copolymer plastomer with an butene content of 30%, an MFI of 70 and a MWD of <4 and made by a metallocene/single site catalyst.

10% of a 50 MFI isotactic or syndiotactic PP homopolymer made using a metallocene/single site catalyst

10% of Fina 3960, a 350 MFI PP homopolymer from Atofina.

This example illustrates the incorporation of a high MFI PP and a low MFI PP compatible polymer into a propylene/butene α-olefin copolymer plastomer ALOP, and which is suitable for the manufacture of thin-walled flexible articles.

Example 11

35% Engage 8401, a 0.885 density, 30 MFI metallocene polyethylene from Dupont Dow

22.55% WSM 168, a 0.919 density, 63 MFI LDPE from Qenos

22.5% WRM 124, a 0.92 density 22 MFI LDPE from Qenos

20% of a 750 MFI PP copolymer

This example illustrates the incorporation of a relatively high (63) MFI LDPE and a relatively low (22) MFI LDPE as components of the ALOP in combination with a high MFI PP copolymer compatible polymer.

Example 12

40% Engage 8407, a 0.87 density, 30 MFI metallocene polyethylene from Dupont Dow
22.55% WSM 168, a 0.919 density, 63 MFI LDPE from Qenos
22.5% WRM 124, a 0.92 density 22 MFI LDPE from Qenos
15% of a 1000 MFI PP homopolymer

This example illustrates the incorporation of a relatively high (63) MFI LDPE and a relatively low (22) MFI LDPE as components of the ALOP in combination with a high MFI PP compatible polymer.

Example 13

90% propylene/butene copolymer with an butene content of 30%, an MFI of 70 and a MWD of <4 and made by a metallocene/single site catalyst.
10% of a 500 MFI polyethylene or ethylene α-olefin copolymer made with a metallocene catalyst.

This example illustrates the incorporation of a high MFI polyethylene or ethylene α-olefin copolymer as the compatible polymer in combination with a propylene/butene α-olefin copolymer. The α-olefin percentage in the copolymer may be varied from 0.5% to 49% depending on requirements of the end use.

Example 14

90% propylene/butene copolymer with a butene content of 30%, an MFI of 150 and a MWD of >4 and made by a metallocene/single site catalyst.
10% of a 500 MFI polyethylene, preferably made by a metallocene/single site catalyst.

This example illustrates the incorporation of a high MFI polyethylene as the compatible polymer in combination with a high MFI polypropylene compatible polymer.

It will be understood by those skilled in the art that the percentages of the various types of blend components illustrated in the above examples may be varied depending on the desired properties of the moulding, and that the range of percentages of the types of blend components that will produce acceptable mouldings may be determined by experimentation.

In terms of ESCR as defined in PCT/AU98/00255, the benefits of the addition of an ALOHMFCP into the ALOP are clearly illustrated by the following examples:

1) A 25:37.5:37.5 blend of SC973:Engage 8401:WSM 168 was injection moulded into tubes and the ESCR tested. SC973 is the compatible polymer in this formulation, and is a 100 MFI PP obtained from Basell. This formulation had a ±30% ESCR failure rate after 360 hours.

2) A 25:37.5:37.5 blend of Atofina 3960:Engage 8401:WSM 168 was injection moulded into tubes and the ESCR tested. Atofina 3960 is the ALOHMFCP in this formulation, and is a 350 MFI PP obtained from Atofina. This formulation showed a 0% ESCR failure rate after 360 hrs as well as significantly improved clarity relative to the comparative formula.

The only difference between formulations 1) and 2) is the substitution of the ALOHMFCP approximately chemical equivalent of the compatible polymer for the compatible polymer, with the key difference between them being the much higher MFI of the ALOHMFCP relative to the compatible polymer. The significant improvement in ESCR performance is due to the much higher MFI (i.e. much lower MW) of the ALOHMFCP relative to the compatible polymer.

In a further development, we have found, surprisingly, that fine, preferably ultrafine and most preferably nanoparticles of a wide variety of non-polymers and polymers may be used as effective compatible agents in the present invention. Preferably the polymer blend of the present invention incorporating fine, preferably ultrafine and most preferably nanoparticles has an MFI>10, preferably >20, more preferably >30 and most preferably >50. Polymers containing nanosized particles of compatible agents are generally referred to as nanocomposites, although the term is more specifically applied to polymer/clay nanocomposites. Without wishing to be bound by theory, we believe that the significant increase in surface area of a given weight of compatible agent when the compatible agent is a fine, ultrafine or nanoparticle form relative the same weight of the same compatible agent in 'non-fine' or larger particle size form causes a significant improvement in ESCR, barrier and other physical properties of the polymer blend of the present invention when such fine, ultrafine or nanoparticles are incorporated into the blend.

Preferably, but not essentially, to obtain optimum results in terms of barrier improvements from nanocomposites of the present invention, the nanocomposite is subjected to high shear during the forming process, such as, for example, injection moulded at high injection speeds. Measuring the injection speed in terms of millimetres of polymer flow down the longest path from the injection point to the point of the moulding furthest from said gates per 0.1 secs of fill time, the injection speed is preferably >35mm/0.1 sec, more preferably >45mm/0.1 sec, yet more preferably >55mm/0.1 sec, even more preferably >65mm/0.1 sec, yet even more preferably >75mm/0.1 sec, still more preferably >95mm/0.1 sec, yet still more preferably >115mm/0.1 sec and most preferably >129mm/0,1 sec.

In blends in which the fine, ultrafine or nanoparticle-sized compatible agent of the present invention is a polymer, the median particle size of the compatible agent when dispersed within a blend is <1000nm (1μm), preferably <700nm, more preferably <500nm, yet more preferably <300nm, even more preferably <200nm, even yet more preferably <100nm, yet even more preferably <75nm and most preferably <60nm and >1nm. Unless otherwise stated, 'particle size' means the mean particle size.

Blends of the present invention containing a fine, ultrafine or nanoparticle-sized compatible agent that is not a polymer or clay, and is preferably a metal oxide such as TiO_2, Zinc oxide, etc. or similar metal compound or metal will have a mean particle size of <200nm, preferably <100nm and most preferably between 4 and 60nm. Typical non-fine TiO_2 such as are extensively used in the plastics industry, such as Dupont TiO2 grades for plastic applications have a mean particle size of 350nm (Grade R960) and 220nm (Grade R104), and so do not fall within the scope of this invention.

Blends of the present invention containing fine, ultrafine or nanoparticle-sized compatible agents that are not a polymer or clay or metal oxide such as are defined above include metal salts such as ultrafine barium sulfate which may have a particle size of 10nm. The present invention can also use as compatible agents particles of other inorganic metal oxides such as those of zinc, electrically conductive tin, e.g., antimony containing tin oxide, iron, zirconium, aluminum, chromium, yttrium, europium, mixtures thereof, among others. The powders have a primary crystallite size of from about 1 to 100 nm, usually from about 4 to about 60 nm. These crystallites can form agglomerates with an average size up to about 300 nm.

Blends in which the fine, ultrafine or nanoparticle-sized compatible agent that is not a polymer and which have the following characteristics also fall within the scope of the present invention:

1) Average particle size between 0.9 and 100nm and an aspect ratio of between 100 and 2000.
2) Preferably the thickness of the nanoparticles is between 0.9 and 100nm and 1500nm (1.5μm wide)
3) Preferably has a thickness of <2nm and a diameter between 10 and 1000nm.

Typically, clays of various types such as are detailed below are preferred compatible agents which may have the above characteristics.

For the purposes of this invention in which clay and similar substances are the compatible agents, measurements refer only to the platelet particle and not any dispersing aids or pretreatment compounds which might be used. Suitable platelet particles are derived from clay materials which are free flowing powders having a cation exchange capacity between about 0.3 and about 3 meq/g and preferably between about 0.8 and about 1.5 meq/g. Examples of suitable clay materials include mica-type layered phyllosilicates, including clays, smectite clays, sodium montmorillonite, sodium hectorite, bentonites, nontronite, beidellite, volkonskoite, saponite, sauconite, magadiite, vermiculite, mica, kenyaite, synthetic sodium hecotorites, and the like. Clays of this nature are available from various companies including Southern Clay Products and Nanocor, Inc.

Layered clay minerals such as smectite clays which are further exemplified by montmorillonite, nontronite, beidellite, volkonskoite, hectorite, saponite, sauconite, magadite, kenyaite and vermiculite are composed of packets of face to face stacking of individual silicate layers or sheets. In nature, the metal ions are substituted for ions such as Mg, Fe, Mn and Li. Because of this substitution, the sheets have a negative charge imbalance that is neutralized by hydratable cations such as sodium and calcium. The thickness of the sheets is about 1 nm and the diameter of the sheets is typically from 50 to 1000 nm resulting in aspect ratios of 50 to 1000. These layered clay minerals are also known as phyllosilicates.

It is known that these layered clay minerals can be treated with organic molecules such as, e.g., organic ammonium ions to insert the organic molecules between adjacent planar silicate layers thereby increasing the interlayer spacing between the adjacent silicate layers. This process is known as intercalation and the resulting treated clay mineral is termed "modified clay" and/or organo-clay. The thus-treated intercalated phyllosilicates have interlayer spacing of at least 1-2nm and up to about 10nm. Depending on the organic molecule used to intercalate the clay, the interlayer spacing may be >10nm, for example, 18-20nm. The modified clay may then be used in at least two distinct methods for preparing nanocomposites, i.e., melt compounding and in situ polymerization. Both methods are known to those skilled in the art. The preferred method of melt compounding of nanocomposites is with a twin-screw extruder or similar blending apparatus. In order to achieve good intercalation, exfoliation and dispersion of the clay minerals, processing conditions should be such that both shear rate and residence time are optimized.

The preferred clays used to form nanoparticles of the present invention are typically smectite clays which are layered phyllosilicates. Smectite clays possess some structural characteristics similar to the more well-known minerals talc and mica. Their crystal structures consist of two-dimensional layers formed by fusing two silica tetrahedral sheets to an edge-shared dioctahedral or trioctahedral sheet of either alumina (for example bentonite) or magnesia (for

example hectorite)--each of the different smectite clays having somewhat different structures. Stacking of these layers in nature in depths of hundreds or more caused by ionic and weak Van der Waals forces leads to voids or chambers between the separate layers. These chambers are occupied by cations which balance the charge deficiency that is generated by isomorphous substitution (often called disharmonies) within the platelet lattices. The platelet particles of the present invention have a thickness of less than about 2 nm and a diameter in the range of about 10 to about 1000 nm. The preferred clays used to prepare an organophilic clay suitable for use in this invention are cation-exchangeable smectite clays which have the cation exchange capacity of at least 75 miliequivalents per 100 grams of clay, 100 percent active basis (i.e. beneficiated and essentially free of non-clay impurities). Smectite-type clays are well known in science, geology and in the art of rheological additives, and are commercially available from a variety of sources both in the United States and throughout the world. They are unique among clays in that they exhibit the phenomena of swelling to many times their size when contacted with water.

Preferred swellable layered clay materials are phyllosilicates of the 2:1 type having a cation exchange capacity of 50 to 200 milliequivalents per 100 grams of mineral. The most preferred swellable layered clay materials are smectite clay minerals, specifically montmorillonite.

Other non-clay materials having the above described ion exchange capacity and size, such as chalcogens may also be used as the source of platelet particles under the present invention. These materials are known in the art and need not be described in detail here.

Nanoparticles, preferably those with very high aspect ratios and particularly, but not exclusively, those consisting of modified clay minerals, can advantageously be used as a compatible agents for the manufacture of injection moulded flexible thin walled articles. When the nanosize particles are clay, they usually have a width of several microns while the thickness is in the nanometers, hence the designation "nanosize" particles. The clay particles are approximately 0.1 to 25% weight percent of the polymer blend, preferably 0.1 to 10.0 weight percent of the polymer blend. Each of the clay particles has a thickness of between 0.9 and 100 nanometers and an aspect ratio of between 100 and 2000, and the polymer may be slightly modified by facilitation agents for the integration of the clay particles.

Preferably the thickness of the nanoparticle ranges between 0.9 and 100nm. The clay platelets may agglomerate to form "tactoids" which increase the thickness of the clay platelets from approximately 0.9nm upwards to 100nm. As is readily apparent, the aspect ratios of the clay platelets of various thickness may be equal if the corresponding widths vary to maintain a similar surface area for each of the clay platelets.

In addition to enhancing the barrier properties of containers, the nanoparticles of the present invention can also enhance the heat stability and mechanical properties of thin walled flexible articles such as containers. An increased heat stability for a container is important in order to allow for "hot-filling" applications. "Hot filling" applications allow for aseptic uses of containers in the food processing industry and also extend the shelf life of various food products. Even small weight percentages of the nanoparticles relative to the polymer material provide substantial increases in the ESCR, impermeability and other physical properties of flexible thin walled articles.

The nanoparticle/polymer blend of the present invention may be fabricated through various methods. One such method is compounding wherein the ingredients are intimately melt-mixed together into as nearly a homogeneous mass as is possible. Using compounding, the clay particles would be melt-mixed with the polyolefin resins. A discussion of compounding is provided in the SPI PLASTICS ENGINEERNG HANDBOOK which relevant parts are hereby incorporated by reference. Other methods of integrating the polyolefin layer include in situ polymerization, solution intercalation and melt exfoliation which are described in U.S. patent application Ser. No. 08/677,282 filed on Jul. 9, 1996 which relevant parts are hereby incorporated by reference.

Nanocomposites are most often prepared today using organically modified silicates or organoclays produced by a cation exchange reaction between the silicate and an alkylammonium salt (usually quaternary ammonium compounds). The alkyl cations exchanged onto the natural clay platelets render the hydrophilic clay organophilic and this transformation makes the clay more easily dispersible into the polymer or plastic. Although excellent sorbents for some organics, natural bentonite and hectorite are themselves very hydrophilic.

The organoclays preferred in this invention differ from ordinary untreated clays in the fact that the untreated clays typically form only ordinary phase-separated mixtures when blended or mixed with a polymer. The clays which are organically modified are more easily dispersed in the polymer matrix and can form a nanocomposite of two types: i.e. intercalated or exfoliated structures. It is preferable to utilize a clay with an exfoliated structure. Intercalated nanocomposites have polymer chains which are intercalated between the silicate layers of the clay resulting in a well ordered multilayer, where the layers of the clay retain their structural registry. Exfoliated nanocomposites are those in which the silicate clay layers or platelets having thickness on a nanometer scale, are exfoliated or separated by various means such as mechanically, by shear mixing, and are randomly and highly dispersed throughout the continuous polymer matrix. It is also possible that nanocomposites can be a mixture having both intercalated and exfoliated structures. In order to obtain better compatibility between the polymer - and particularly polyolefin polymers - and the organoclay, it is often desirable that the organoclay contains substituted alkyl side chains.

The organic cations which can be reacted with a clay to form the organically modified clay utilized in the present invention can be selected from a variety of organic molecules, preferably nitrogen-based quaternary materials that are capable of exchanging cations with the selected smectite-type clays in particular. The organic cations which are reacted with the smectite-type clay to prepare organophilic clays have may preferably a positive charge localized on a single nitrogen atom within the compound. Preferably the organic cation is provided by specific quaternary ammonium compounds derived in whole or in part from organic acid-derived esters. A further detailed description of organoclay compositions which are suitable for use in the present invention can be found in U.S. Pat. Nos. 5,718,841 and 4,434,075 which are fully incorporated herein by reference.

Suitable non-limiting organoclays for use in the present invention are available from Southern Clay Products, of Gonzales, Tex., under the trademark Cloisite 15A, Cloisite 20A, and SCPX--1967, from Nanocor, Inc. of Arlington Heights, Ill., tradename Nano #405, and from Rheox, Inc. (Elementis Specialties) of Hightstown, N.J., available as Rheox EA108, EA2827, EA2885, EA2886. Preferred organoclays are available from Rheox as EA2827 and EA2886.

Included in this invention are clay/organic chemical compositions that consist of an organic chemical/clay intercalate, preferably an organic chemical/smectite clay intercalate, that has been ion-exchanged and reacted with one or more quaternary ammonium compounds. This composition is designated as a hybrid organoclay. Since such a hybrid organoclay is hydrophobic, it can be washed with water after manufacture to remove reaction salts and excess water soluble or water dispersible organic material to give a clean product via inexpensive means such as filtration. This allows a better dispersing composition to be prepared without the difficulties of isolation presented by many other techniques which use energy intensive means to remove the bulk of the water from the final product and cannot be easily washed.

In one aspect, the nanoparticles of present invention are a clay/organic chemical composition that comprises: (a) one or more smectite clays, (b) one or more quaternary ammonium compounds which react via an ion exchange mechanism with the clay, and (c) one or more defined non-anionic organic materials that are intercalated with the smectite clay.

The compositions of the present invention comprise between about 0.01 and about 25 wt %, preferably between 0.5 and 25 wt %, more preferably between 0.5 and 15 wt % and most preferably between 0.5 and 10 wt % of at least one certain expanded organoclay which is derived from organic and inorganic clay materials.

In the present invention, and when a clay is used as the nanoparticle, it is often desirable to use an organically modified clay, or organoclay which will form a nanocomposite with the polymer blend. The organically modified clays are generally prepared by reacting a clay with an organic cation or cations provided by specific quaternary ammonium compounds. The polymer such as a polyolefin and an organoclay are intimately mixed and dispersed on a microscopic or nanoscale level resulting in a composition having increased heat and flame resistance. The organo clays of the present invention generally have a particle size from about 1 to about 10,000 nanometers, desirably from about 100 to about 2,000 nanometers, and preferably from about 200 to about 500 or 1,000 nanometers.

When the main polymer to be used to form the nanocomposite is a polyolefin, it has been found that, all other things being equal, the greater the degree of short-chain branching in the polymer (as measured by SCBI) the greater the extent of exfoliation of the organoclay, and hence the better the overall properties of the nanocomposite. Similarly, in the case of olefin α-olefin and other copolymers, the greater the percentage of α-olefin or other copolymer in the polymer, the greater the extent of exfoliation of the nanocomposite. Also, polymers exhibiting super-random distribution of the monomers within the polymer molecules are particularly suited to the production of nanocomposites of the present invention as their use tends to give greater degrees of exfoliation than similar polymers not exhibiting super-random distribution of the monomers. Such super-random polymers may be catalysed by metallocene or similar catalysts which are well known in the art.

There are a wide variety of methods that can be used to prepare nanoparticles suitable for use as compatible agents. Ophir et l, WO 02/079318, provides a provides a process for making nanocomposite plastic material, which comprises the following steps: a) providing a polyolefin material; b) providing virgin Montmorillonite; c) subjecting the Montmorillonite to intercalation; d) preferably, mixing the intercalated Montmorillonite with a compatibilizer capable of improving the compabitility of the intercalated clay with the plastic material of the

nanocomposite, preferably a polyolefin plastic materials, to form a concentrate; and . e) compounding the resulting mixture with the said polyolefin material, resulting in the separation of the Montmorillonite platelets from one another, viz. in their exfoliation. The intercalation of the Montmorillonite to bring it to such a condition that it may later be exfoliated and compounded with the matrix polyolefin, or, preferably, with a compatibilizer, is preferably carried out with an epoxy resin, such as bisphenol A, though other intercalants, such as silanes, may be used. The compound used to produce intercalation - the "intercalant" must be capable of insinuating itself between the platelets of the Montmorillonite galleries and to interact with the attractive forces that exist in the galleries to distance the platelets from one another, but must also be capable of the interconnecting with the compatibilizer, hereinafter to be described. In order to become insinuated between platelets, the intercalant should preferably be brought to a condition of low viscosity. The next preferred step of the process of the invention is the creation of a concentrate which is mixture of intercalated Montmorillonite with a compatibilizer, which is preferably a polyolefin grafted with a functional compound that will permit it to penetrate between the platelets that have. undergone the intercalation. A preferred compatibilizer is a polyolefin grafted with maleic anhydride. The amount of compatibilizer used is 5 to 10 wt of the amount of the polymer matrix of the final composite. The concentrate is to be mixed with the polymer of the matrix by, for example, separate compounding, or preferred by mixing the concentrate directly with the matrix polymer and subjecting the mixture to the operation by which the final product is formed. This formation of the final product results in the exfoliation of the clay to form the exfoliated nanopolymer. Additionally, in an embodiment of the invention, another polar compound compatibilizer, preferably based on a nylon, intercalated with Montmorillonite, can be added to the mixture of matrix polymer and intermediate stabilizer, also in a quantity, e.g., from 5 to 10% wt of the amount of the matrix polymer.

The ratio of thickness to length varies between 300 to 1500 and one gram of the Montmorillonite platelets has a surface area of approximately 750 square meters. The type of intercalant and the quantity introduced into the clay stack will determine the distance between layers of the Montmorillonite. It is well known that different intercalants result in different degrees of exfoliation, as is illustrated in US 6232388, which demonstrates that an octadecyl amine onium clay intercalant produces significantly better nylon-based nanocomposite barrier films compared to the same polymer nanocomposite in which the clay intercalant is an n-alkyl dimethyl benzyl amine onium ion As the distance between plates grows, the force holding the structure together diminishes until the point at which placing the nano-clay into the matrix of a polymer and applying mechanical shearing forces will cause the plates of the nano-clay to undergo exfoliation. In a preferred embodiment of this invention, an epoxy resin such as bisphenol A is used as an intercalant. In order to introduce the epoxy resin into the galleries of the agglomerate, it is preferable to reduce the viscosity of the resin. This can be accomplished by applying it as a solution of concentration 5 to 10 wt in chloroform.

There are two ways to perform the exfoliation step. In the first method, an appropriate intercalant is introduced into the galleries of the Montmorillonite. This intercalant must be capable of expanding the galleries enough to allow polymer macromolecules to enter the gallery. During the polymerization reaction, the space between the layers of the Montmorillonite is further increased until the force holding the structure together is so weakened that exfoliation takes place. The intercalant also should preferably have a functional group that can interact with the polymer during the reaction and effectively link the platelets to the polymer. Nanocomposites produced in this way have improved

mechanical properties when compared to their polymer matrix, which render them superior to said matrix, but their resistance to seepage of liquids and gases is not optimal, due to the random orientation of the clay platelets in the polymer matrix. However, when said resistance is an essentially desired property, the final product is made by extrusion or injection processes and the shearing forces that are present in such processes cause delamination of the layers in the Montmorillonite and assist in the exfoliation process.

The following examples are illustrative and not limitative. The process of the examples is divided into four steps, which will be successively described. In the first step virgin Montmorillonite powder is subjected to intercalation. In the second step the powder obtained from step 1 is mixed with compatibilizer polymers and compounding is carried out to produce a concentrate. In this step intercalation is completed and partial exfoliation is effected. The third stage is a melt blending stage in which the concentrate or concentrates of the second step is/are compounded with the polyolefinic matrix and a complete exfoliation takes place. In the fourth and final step, a melt of the mixture obtained from the third step is subjected to a combined process of elongation and shear which produces the orientation of the mineral particles.

US 5910523 describes composites from a semi-crystalline polyolefin and nanometer sized fillers with improved modulus, tensile strength and crack growth resistance are disclosed. The nanometer sized fillers are first functionalized with an aminosilane. Thereafter, a carboxylated or maleated polyolefin is grafted to the filler through an amine-carboxyl reaction. The resulting modified filler is dispersed in a semi-crystalline polyolefin (eg. polyethylene or polypropylene). Co-crystallization between the carboxylated or maleated polyolefin and the semi-crystalline polyolefin can improve interaction between the filler and semi-crystalline polyolefin.

Alexandre, et. al., WO 99/47598, disclose a nanocomposite which is a dispersion of nanofiller particles derived from layered metal oxides or metal oxide salts. The nanocomposite is advantageously prepared by first swelling an untreated clay in water, then removing the water to form an organophilic clay that is dispersible in non-polar organic solvents. The organophilic clay can then be treated with an alkyl aluminoxane and subsequently a catalyst, including Ziegler-Natta and metallocene catalysts,to form a complex that promotes olefin or styrenic polymerization and platelet dispersion. The nanocomposite can be prepared directly by in situ polymerization of the olefin or the styrene at the nanofiller particles without shear, without an ion exchange step, and without the need to incorporate polar substituents into the polyolefin or polystyrene.

Elspass et al, US 5,883,173 discloses a method for producing nanocomposites by dispersing a clay in water containing a surfactant, adding polymerisable monomer or monomer, and a polymerisation initiator to the mixture and then polymerising the monomer to form a latex. The latex can also be formed from preformed polymers. Composite materials formed from latexes produced by either method have improved mechanical properties and reduced air permeability.

Fischer, et al., WO 99/35185 disclose a method for preparing a nanocomposite material based on a polymeric matrix and a layered double hydroxide. Barbee, et al., WO 99/32403 disclose a composition comprising a polymer having dispersed therein at least one layered clay material which has been cation exchanged with organic cation salts; and at least one

expanding agent which is compatible with said polymer. The compositions of the disclosure show vastly improved platelet separation as evidenced by higher than previously reported basal spacing. Fischer, WO 99/07790 discloses a nanocomposite material on the basis of a clay having a layered structure and a cation exchange capacity of from 30 to 250 milliequivalents per 100 grams, a polymeric matrix and a block copolymer or a graft copolymer, which block copolymer or graft copolymer comprises one or more first structural units, which are compatible with the clay, and one or more second structural units, which are compatible with the polymeric matrix. Fischer further discloses a nanocomposite material wherein the clay has a cation exchange capacity of from 50 to 200 milliequivalents per 100 gram. In addition, Fischer discloses a nanocomposite material wherein the polymeric matrix is selected from the group consisting of polyolefins, vinyl polymers, polyesters, polyethers, polysiloxanes and acrylic polymers. Li, et al., WO 98/53000 disclose toughened nanocomposite materials which are prepared based on a blend of one or more thermoplastic engineering resins, e.g., nylon, a functionalized, e.g., brominated, copolymer of a C.sub.4 - C.sub.7 isomonoolefin, e.g., isobutylene, and a para-alkylstyrene, e.g., para-methylstyrene, and further contain a uniformly dispersed exfoliated phyllosilicate layered clay, e.g., montmorillonite. The nanocomposite materials exhibit superior mechanical properties, including enhanced impact strength.

Matayabas, et al., WO 98/29499 disclose polyester-platelet particle composite compositions comprising about 0.01 to about 25 weight percent platelet particles dispersed in at least one polyester. Frisk, et. al., WO 98/01346 disclose a container which is composed of a polymer material integrated with a plurality of nanosize particles of a clay mineral which act to enhance the barrier properties of the container. The nanocomposite polymer containers of the disclosure are able to accomplish this due to the minimal amount of clay integrated with the polymer material, i.e., between 0.1% and 10% weight of the container. The small amount of clay provides a substantial barrier due to the high aspect ratios of the clay particles which will vary between 100 and 2000. The nanocomposite polymer container may be produced using in situ polymerization, solution intercalation, or melt exfoliation to integrate the clay mineral with the polymer material matrix. The clay mineral may be smectite, vermiculite, halloysite or any synthetic analog thereof, with a preference for the montmorillonite species of smectite clays.

The amount of modified clay material combined with the polymer should be in an amount that is sufficient to provide the desired ESCR, barrier and/or mechanical properties. The amount of modified clay material in the nanocomposites of the invention comprises about 0.1% to about 25% by weight of the composition. A preferred range of modified clay material comprises about 0.5% to about 10% of the composition.

Polymers suitable for use in the nanocomposites of the present invention are exemplified, but not limited to, ALOPs as defined herein, including polymers such as polyolefins, including plastomers, substantially linear metallocene polyethylene α-olefin copolymers, low density polyethylene (LDPE), linear low density polyethylene (LLDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), isotactic, syndiotactic and atactic polypropylene (PP) such as polypropylene with varying degrees of isotacticity such as are described in, amongst others, WO 01/27169 (P&G), WO/99/52955 (Rieger), WO 99/52950 (Rieger) and WO/99/29749 (ExxonMobil), α-olefin copolymers of ethylene, propylene or butene, preferably α-olefin copolymers of ethylene, propylene or butene prepared using metallocene or similar catalysts capable of producing super-random distribution of the α-olefin copolymer within and amongst the molecular chains, polyamides such as poly(m-

xyleneadipamide) (MXD6), poly(hexamethylenesebacamide), poly(hexamethyleneadipamide) and poly(-caprolactam), polyesters such as poly(ethylene terephthalate), and polyacrylonitriles. Other polymers suitable for use in the nanocomposites of the invention include ethylene vinyl alcohol copolymers, ethylene vinyl acetate copolymers, polyesters grafted with maleic anhydride, PVdC, aliphatic polyketone, and LCP (liquid crystalline polymers). A polyketone is exemplified by Carillon.RTM. which is produced by Shell. A liquid crystalline polymer is exemplified by Vectra.RTM. which is produced by Ticona. Further polymers that may be used include epoxy and polyurethane adhesives.

While certain clay minerals have been exemplified above it is understood that any clay mineral (both natural and synthesized) a large contact area with the polymer to be used in said nanocomposite are useful in the present invention.

Definition of Terms:
Unless specifically set forth and defined or otherwise limited, the following terms as used herein have the following meanings.

Aspect Ratio shall mean the ratio of a particular object's width to its thickness.

Exfoliate or exfoliated shall mean individual platelets of a modified clay so that adjacent platelets of the modified clay can be dispersed individually throughout a carrier material, such as water, a polymer, an alcohol or glycol, or any other organic solvent.

Exfoliation shall mean a process for forming an Exfoliate from a modified clay.

Intercalant shall mean an organic molecule such as an ammonium ion that is absorbed between platelets of the layered material and complexes with the Na.sup.+ cations on the platelet surfaces to form an Intercalate.

Intercalate or intercalated shall mean a Layered Material that includes organic molecules disposed between adjacent platelets of the Layered Material to increase the interlayer spacing between the adjacent platelets to at least about 0.5nm., preferably at least about 1nm.

Intercalation shall mean a process for forming an Intercalate.

Layered Material shall mean an inorganic material, such as a smectite clay mineral, that is in the form of a plurality of adjacent, bound layers and has a thickness, for each layer, of about 0.3 to 5nm, preferably about 1nm.

Matrix monomer shall mean a monomer that the Intercalate or Exfoliate is mixed with or dispersed.

Matrix polymer shall mean a thermoplastic or thermosetting polymer in which the Intercalate and/or Exfoliate is mixed or dispersed to form a Nanocomposite.

Modified clay shall mean layered material that has undergone intercalation.

Nanocomposite shall mean a mixture that includes a monomer, polymer, oligomer, or copolymer having dispersed therein a plurality of individual platelets obtained from an exfoliated modified clay.

Platelets shall mean individual layers of the Layered Material.

Smectite is a 2:1 type layer silicate with an expandable lattice carrying an excess negative layer charge. The 2:1 ratio refers to a layered structure consisting of an octahedral metal oxide sheet sandwiched between two tetrahedral silicon oxide sheets.

Carbon-carbon double bonds are particularly susceptible to reaction with the intermediate species. Such carbon-carbon bonds are often found in foods and beverages, pharmaceuticals, dyes, photochemicals, adhesives, and polymer precursors. Virtually any product which has complex organic constituents will contain such carbon-carbon double bonds or other oxygen reactive components, and hence can undergo oxidative reactions. Thus, if the oxidation products adversely affect the performance, odor or flavor of the product, then removing the oxygen which is present (either dissolved in or trapped with the product), preventing oxygen ingress, or inhibiting the reactions of oxygen will benefit the product.

In a further development, we have found that the incorporation of oxygen scavengers into nanocomposites significantly enhances the oxygen barrier properties of nanocomposites for a wide variety of applications, including films and other articles made by extrusion or casting, injection stretch, injection blow, thermoforming and other plastic manufacturing processes well known to those skilled in the art. The development of nanocomposite/oxygen scavenger compositions of the present invention is particularly, but not exclusively, suited to the injection moulding of flexible thin walled articles where enhanced oxygen and other barrier properties are required. All nanocomposites, irrespective of polymer type, are suitable for use with this invention. For example, polyamides such as the various nylon polymers, polyesters such as PET and PEN, polycarbonates and polyolefins are particularly suited for use with the present invention. Polyolefins of various types in particular, by virtue of their relatively low cost and easy processability, are advantageously used in the present invention, and the very good barrier and oxygen scavenging properties of the invention relative to 'standard' polyolefins, polyolefin nanocomposites and polyolefins containing oxygen scavengers when used alone enables the use of polyolefins for applications requiring barrier, particularly to oxygen, for which the aforementioned polyolefins and compositions thereof are unsuitable.

Although the following discussion uses mainly polyolefin nanocomposite/oxygen scavenger compositions to illustrate the present invention, it will be understood that the same principles apply to other polymer types that can be compounded to produce nanocomposite/oxygen scavenger compositions, and which are therefore included in the present invention. The term 'polyolefin' may therefore be substituted by, for example, polyester, polyamide, etc. Therefore with the aforementioned in mind, the present invention includes:

- Polyolefin/nanocomposite/oxygen scavenging compositions
- Polyolefin/nanocomposite/oxygen scavenging compositions used for injection moulding applications
- Polyolefin/nanocomposite/oxygen scavenging compositions used for injection moulding flexible thin-walled articles as defined herein
- More particularly polyolefin/nanocomposite/oxygen scavenging compositions having an MFI>10, preferably >20, more preferably >30 and most preferably >50

- Yet more particularly polyolefin/nanocomposite/oxygen scavenging compositions having polymer components with MFI>10, preferably >20, more preferably >30 and most preferably >50.
- Yet more particularly polyolefin/nanocomposite/oxygen scavenging blends having polymer components with MFI>10, preferably >20, more preferably >30 and most preferably >50 and incorporating compatible agents and/or polymers for improved ESCR and barrier performance.
- Preferably when using the present invention for the manufacture of thin walled flexible articles, when measuring the injection speed in terms of millimetres of polymer flow down the longest path from the injection point to the point of the moulding furthest from said gates per 0.1 secs of fill time, the injection speed is preferably >35mm/0.1 sec, more preferably >45mm/0.1 sec, yet more preferably >55mm/0.1 sec, even more preferably >65mm/0.1 sec, yet even more preferably >75mm/0.1 sec, still more preferably >95mm/0.1 sec, yet still more preferably >115mm/0.1 sec and most preferably >129mm/0,1 sec.

Such compositions are particularly suited to the injection moulding of flexible thin walled articles, and the nanocomposite/oxygen scavenging compositions display synergistic benefits with regard to barrier properties (measured as OTR) relative to the same essential compositions but in which the nanocomposite and oxygen scavenging components feature as separate components. The compositions may be prepared by a variety of means, such as by mixing the blend the components under high shear mixing conditions or other means capable of producing an intimate mix, such as in a twin-screw extruder. The nanocomposite/oxygen scavenger blend may also be produced by first preparing a nanocomposite and then as a separate step compounding the oxygen scavenger into the nanocomposite. Alternatively, the polymer/oxygen scavenger blend may be prepared and the organo-clay, or masterbatch thereof, subsequently compounded into the polymer/oxygen scavenger blend. Other means to achieve a well mixed blend will be apparent to those skilled in the art.

In another variation on the present invention, by selecting appropriate intercalants for the preparation of the organo-clay component of the nanocomposite to be used in the nanocomposite/oxygen scavenger blend of the present invention, it is possible to use as the intercalant a molecule that can also act as an oxygen scavenger. This may be achieved by, for example, selecting as an intercalant an organic molecule that has oxygen scavenging properties or by grafting, polymerising or otherwise incorporating an oxygen scavenging functional group(s) onto a 'standard' (i.e. non-oxygen scavenging) intercalant

US 6423776 describes the effects of incorporating an oxygen scavenger into a polyamide/nanocomposite film. However, it does not describe any benefits to the use of polyolefin/nanocomposite/oxygen scavenging compositions, nor the use of a nanocomposite/oxygen scavenger combination in relatively high MFI compositions that are suitable for injection moulding, and particularly for injection moulding of flexible thin walled articles.

For the purposes of this invention, the term polyolefin means a polymer whose molecular makeup consists of more that 50% of an olefin such as ethylene, propylene, butene. In other words, more than 50% of the number of monomer molecules that are polymerised to make the polymer are olefins. Preferably the polyolefin is a low molecular weight plastomer, 'substantially linear polyethylene, metallocene long-chain branched polyethylene or copolymer of the aforementioned ethylene polymers, linear or branched isotactic or

syndiotactic polymers, particularly polypropylene and polybutene homopolymers or random copolymers, including linear or branched isotactic or syndiotactic polypropylene or polybutene homopolymers or random copolymers which have a structure in which their tacticity varies within the range of between 25 and 60% of [mmmm] pentad concentration. Also suitable for use in the present invention are linear or branched isotactic polymers having an arbitary or rather regular sequence of isotactic and atactic blocks within the polymer molecules.

When the main polymer to be used to form the nanocomposite is a polyolefin, it has been found that, all other things being equal, the greater the degree of short-chain branching in the polymer (as measured by SCBI) the greater the extent of exfoliation of the organoclay, and hence the better the overall properties of the nanocomposite. Similarly, in the case of olefin α-olefin and other copolymers, the greater the percentage of α-olefin or other copolymer in the polymer, the greater the extent of exfoliation of the nanocomposite. Also, polymers exhibiting super-random distribution of the monomers within the polymer molecules are particularly suited to the production of nanocomposites of the present invention as their use tends to give greater degrees of exfoliation than similar polymers not exhibiting super-random distribution of the monomers. Such super-random polymers may be catalysed by metallocene or similar catalysts which are well known in the art.

There are many oxygen scavenging systems that are suitable for use in the nanocomposite/oxygen scavenger compositions of the present invention. Some of these are described below, but other systems not described may also be suitable. The suitability of a particular system may be determined by experimentation, as may the optimum type of nanocomposite to be used in conjunction with a particular oxygen scavenger(s) in the invention. Various types of nanocomposites and various methods for their preparation are described above, but it will be understood that the types and methods described are non-limiting.

US 5,492,742 (Zenner) describes oxygen scavenging packages and containers which comprise a composition of a carrier, such as a polymer, which is permeable to both oxygen and water or water vapour and an oxygen scavenging compound of an organic compound or salt thereof dispersed relatively uniformly throughout the polymer in an amount effective to act as an oxygen scavenger. The oxygen scavenging compound is a salicylic acid chelate or complex of a transition metal or a salt thereof. The oxygen scavenging composition is activated for scavenging oxygen by contact with water or water vapour which permeates into or through the carrier. A reducing agent of an ascorbate compound may be added to enhance the performance of the salicylic acid chelate or complex. The oxygen scavenging compound may be added to the composition in a dry state, and is inactive until activated for oxygen scavenging by contact with water or water vapour.

There is a need for a material or product which can rapidly reduce oxygen levels inside a package of products which are wet or moist (or which are capable of generating moisture inside their packaging) without adversely changing taste, aroma, or functionality of such packaged foodstuffs, beverages and pharmaceuticals. Persons skilled in the art have considered the addition of various agents into the packaging of such products in an attempt to meet this need.

Japanese patent application 61-238,836 discloses a packaging film made from a thermoplastic such as low density polyethylene ("PE"), which includes ascorbic acid alone or

in combination with an aliphatic polycarboxylic acid. This film is disclosed as having good gas barrier properties.

Japanese patent application 54-022,281 discloses a fruit tray made of a thermoplastic foam base having a thin layer of ascorbic acid or erythorbic acid (or one of their alkali metal salts) on the face of indentations in the tray upon which the fruit is to be placed.

Salicylic acid complexes and their reactivities towards oxygen are generally known and are described in Zanello et al., Inorganica Chim. Acta 1983, vol. 74, pp. 89-95 and Cini et al., Inorganica Chim. Acta 1984, vol. 88, pp. 105-113.

In one embodiment of the invention, the oxygen scavenging composition comprises a carrier, such as a polymer, preferably a thermoplastic polymer, which is permeable to oxygen and water or water vapour; and a transition metal complex or chelate of a salicylic acid or a salicylate salt, whether or not substituted, dispersed relatively uniformly through the carrier and added in an amount sufficient to act as an effective-oxygen scavenger.

The transition metal of the chelate is preferably iron, copper, cobalt, or nickel; most preferably it is either iron or copper. The transition metal used to make the chelate or complex may be supplied as a simple salt, such as iron or copper chloride, iron or copper sulfate, iron gluconate, nickel sulfate, or cobalt chloride, but is present as part of the chelate or complex.

It is also possible, and in some cases preferred, to include a reducing agent, such as an ascorbate compound, in the polymer in an amount sufficient to enhance, preserve or augment the oxygen scavenging properties of the transition metal chelate or complex. Ascorbic acid, in its D- or L- form, or a derivative, analog or salt thereof, may be used as a preferred reducing agent, since it also has oxygen scavenging properties.

The oxygen scavenging material is uniformly dispersed in and throughout the carrier by a direct mixing technique. Advantageously, the oxygen scavenging material is mixed or blended into the carrier in a dry state. The oxygen scavenging capabilities of these compositions are later activated by contact with water or water vapour which permeates into or through the carrier.

US 5,641,825 (Bacskai) describes a composition of matter having oxygen scavenger capabilities. The composition comprises a blend of a first polymeric component comprising a polyolefin, the first polymeric component having been grafted with an unsaturated carboxylic anhydride or an unsaturated carboxylic acid, or combinations thereof, or with an epoxide; a second polymeric component having OH, SH or NHR.sup.2 groups where R.sup.2 is H, C.sub.1 -C.sub.3 alkyl, substituted C.sub.1 -C.sub.3 alkyl; and a metal salt capable of catalyzing the reaction between oxygen and the second polymeric component, the polyolefin being present in an amount sufficient so that the blend is non phase-separated. In the preferred composition maleic anhydride is the grafted material, the second polymeric component is MXD6 nylon and the metal is cobalt. A method of providing a homogeneous blend of a polyolefin with a second polymeric component having OH, SH or NHR.sup.2 groups is also set forth. Articles such as containers for foods and beverages utilizing such compositions and/or such method are provided.

US 5,952,066 is directed to the novel use of an aliphatic polyketone as an oxygen scavenger in a structure for the packaging of oxygen-sensitive products. In contrast to the prior art which would modify the aliphatic polyketone to render it less reactive with and less permeable to oxygen, this invention utilizes the polymer's high oxygen reactivity to effectively capture any oxygen which may enter the product and thus enhance the shelf life. As an additional benefit, the carbon dioxide (CO.sub.2) which builds up in the package sidewall (as a degradation product) would be expected to reduce the migration of CO.sub.2 from the food product.

In another embodiment, a monolayer transparent package is provided wherein an aliphatic polyketone is blended or copolymerized with other polymers. For example, a blend comprising 0.1 to 10% by total weight of a polyketone terpolymer scavenger, and the remainder PET, is used to form an injection molded preform and transparent expanded preform beverage bottle. At relatively low levels, the polyketone polymer remains amorphous and the container substantially transparent (in contrast to the highly crystalline and opaque barrier polyketone proposed in the art). In this embodiment, the terpolymer may scavenge oxygen from the container based on direct food contact with the product.

It is possible to introduce a second olefinic monomer into the polymerization, such as propylene, which will substitute randomly for ethylene, and in alternation with carbon monoxide, to produce the terpolymer poly(ethylene-alt-carbon monoxide)-stat-(propylene-alt-carbon monoxide) (hereinafter E/P/CO terpolymer. E/P/CO is just one example of a terpolymer, there being many other possible terpolymers with varying properties. Alternatively, it is possible to introduce one or more other olefin monomers that will copolymerize, such as acrylates, methacrylates, alkyl compounds, vinyl acrylate, vinylsilanes, vinyl chloride, etc. Additives such as aldol blocking agents, lubricants, release agents, etc. may be used to enhance processing properties and to reduce the tendency for aldol condensation.

US 6,254,804 discusses a variety of oxygen scavenging materials that have been incorporated directly into the packaging structure. This technique (hereinafter referred to as "active oxygen barrier") can provide a uniform scavenging effect throughout the package and can provide a means of intercepting and scavenging oxygen as it passes through the walls of a package, thereby maintaining the lowest possible oxygen level throughout the package. Active oxygen barriers have been formed by incorporating inorganic powders and/or salts as part of the package. See, e.g., U.S. Pat. Nos. 5,153,038, 5,116,660, 5,143,769, and 5,089,323.

EP 0 519 616 discloses an oxygen scavenging composition that includes a blend of an epoxide, a first polymeric component grafted with an unsaturated carboxylic anhydride and/or acid, a second polymeric component including OH, SH, or NHR.sup.2 groups where R.sup.2 is H, C.sub.1-C.sub.3 alkyl, or substituted C.sub.1 -C.sub.3 alkyl moiety, and a metal salt capable of catalyzing the reaction between oxygen and the second polymeric component. The first polymeric component is present in an amount sufficient to ensure that the blend is non-phase separated. A blend of polymers is utilized to obtain oxygen scavenging, and the second polymeric component is preferably a (co)polyamide such as MXD6.

Another type of active oxygen barrier is illustrated in EP-A-0 301 719, EP-A-0 380 319, PCT publication no. WO 90/00578, and PCT publication no. WO 90/00504. See also U.S. Pat. Nos. 5,021,515, 5,194,478, and 5,159,005. The disclosed oxygen scavenger includes polyamide-transition metal catalyst compositions. Through catalyzed scavenging by the

polyamide, the package wall regulates the amount of oxygen reaching the interior of the package.

Oxygen scavenging compositions that include transition metal catalysts and ethylenically unsaturated hydrocarbon polymers which have an ethylenic double bond content of from 0.01 to 10 equivalents per 100 grams of polymer are disclosed in U.S. Pat. No. 5,399,289. Various conventional homopolymers, copolymers, and polymer blends are disclosed.

The use of a transition metal and a photoinitiator to facilitate initiation of effective scavenging activity of ethylenically unsaturated compounds is taught in U.S. Pat. No. 5,211,875, which is incorporated herein by reference as if set forth in full.

PCT publication nos. WO 95/02616 and WO 96/40799 disclose a scavenger composition that includes a transition metal salt and a copolymer (of ethylene and a vinyl monomer) having ether, amino, carboxylic acid, ester, or amide functionalities pendent therefrom. PCT Application WO 96/40799 describes the use of a variety of ethylenic materials with benzylic, or ether containing side chains. Some of these materials may be prepared by esterification or transesterification of a polymer melt. The use of pendent cyclic groups containing unsaturation is generally referred to.

Accordingly the patent in question seeks to address the problems associated with scission products of oxygen scavengers, and seeks also to provide a group of compounds and substances (as well as films and plastic materials including same) which have an advantage over the prior art in terms of reduced quantities of scission products.

Ideally, a polymeric material for use in an oxygen scavenging composition should exhibit good processing characteristics, be able to be formed into useful packaging materials or have high compatibility with those polymers commonly used to make packaging materials, and not produce byproducts which detract from the color, taste, or odor of the packaged product. It has been found that when the ethylenic unsaturation is contained within a cyclic group, substantially fewer and less byproducts are produced upon oxidation as compared to analogous non-cyclic materials. Optimally, a packaging material formed from such a composition can retain its physical properties after significant oxygen scavenging. Oxygen scavenging compounds for use in plastic films are relatively well known.

It has been found that materials containing certain cyclohexenyl functionalities are excellent oxygen absorbers when compounded with a transition metal salt and optionally a photoinitiator, and that when these materials oxidize they produce very low levels of oxidation byproducts. This is in marked contrast to the known art, where excellent oxygen absorbers can be obtained from the use of linear unsaturated compounds compounded with a transition metal salt, and a photoinitiator, but where the levels of oxidation byproducts are excessively high. It is thought that this improvement is obtained because mild oxidation of cyclohexene does not break bonds on the ring structure whilst oxidation of a linear unsaturated material such as linoleic acid or vegetable oil under similar conditions produces smaller molecules by chain scission. When incorporated into polymers, the cyclohexene containing systems are found to produce considerably less volatile byproducts than the linear unsaturated materials.

The compositions of this invention are significantly cleaner than those described in the prior art, they do not require the use of high levels of adjuncts to absorb the undesirable

byproducts. Such absorbent additives are known in the art, for example see U.S. Pat. No. 5,834,079 and U.S. 08/857,276. It is also well know in the art that such additives (zeolites and silicas) adversely effect the haze and clarity of packaging structures.

The oxygen scavenging composition of the invention comprises:

(a) a polymer or lower molecular weight material containing substituted cyclohexene functionality.

(b) a transition metal catalyst; and optionally

(c) a photoinitiator. Suitable photoinitiators are known to those skilled in the art. See, e.g., PCT publication WO 97/07161, WO 97/44364, WO 98/51758, and WO 98/51759 the teachings of which are incorporated herein by reference as if set forth in full.

In combination with the polymeric component, the oxygen scavenging composition of the present invention includes a transition metal compound as an oxygen scavenger catalyst. The transition metal catalyst can be a salt which includes a metal selected from the first, second, or third transition series of the Periodic Table.

One or more antioxidants can be incorporated into the scavenging composition of the present invention to retard degradation of the components during compounding and film formation. Although such additives prolong the induction period for oxygen scavenging activity to occur in the absence of irradiation, the layer or article (and any incorporated photoinitiator) can be exposed to radiation at the time oxygen scavenging properties are required. Suitable antioxidants include 2,6-di(t-butyl)-4-methylphenol (BHT), 2,2'-methylene-bis(6-t-butyl-p-cresol), triphenylphosphite, tris-(nonylphenyl)phosphite, dilaurylthiodipropionate, vitamin E (.alpha.-tocopherol), octadecyl 3,5,-di-tert-butyl-4-hydroxyhydrocinnamate, tetrakis[methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)]methane and the like.

When an antioxidant is included as part of the composition of the present invention, it preferably is present in an amount which prevents oxidation of the components of the oxygen scavenging composition as well as other materials present in a resultant blend during formation and processing; however, the amount preferably is less than that which interferes with the scavenging activity of the resultant layer, film, or article after initiation has occurred. The amount needed in a given composition can depend on the components present therein, the particular antioxidant used, the degree and amount of thermal processing used to form the shaped article, and the dosage and wavelength of radiation applied to initiate oxygen scavenging. Typically, such antioxidant(s) are used in an amount of from about 0.01 to about 1% (by wt.).

Other additives that also can be included in the oxygen scavenging composition of the present invention include, but are not necessarily limited to, fillers, pigments, dyestuffs, processing aids, plasticizers, antifog agents, antiblocking agents, and the like.

The composition of the present invention can provide oxygen scavenging properties at a desirable rate and capacity while having good processing and compatibility properties relative to compositions including conventional non-cyclic ethylenically unsaturated polymers. Thus, the present composition can be used to provide, by itself or as a blend with diluent polymers such as polyolefins and the like, a packaging material or film that can be

manufactured and processed easily. Further, the subject oxygen scavenging composition will deplete the oxygen within a package cavity without substantially detracting from the color, taste, and/or odor of the product contained therein.

The amount of the polymeric scavenging component contained in the subject composition can range from about 1 to almost about 100%, preferably from about 5 to about 97.5%, more preferably from about 10 to 95%, even more preferably from about 15 to about 92.5%, still more preferably from about 20 to about 90%, (with all of the foregoing percentages being by weight) of the composition or layer made therefrom. Typically, the amount of transition metal catalyst can range from 0.001 to 1% (by wt.) of the scavenging composition, based on the metal content only (i.e., excluding ligands, counterions, etc.). Where one or more other scavenging compounds and/or diluent polymers are used as part of the composition, such other materials can make up as much as 99%, preferably up to about 75%, by weight of the scavenging composition. Any further additives employed normally do not make up more than 10%, preferably no more than about 5%, by weight of the scavenging composition.

US 6274210 describes an improved oxygen scavenging composition and packaging container formed therefrom. The container is suitable for storage of oxygen sensitive materials and has as part of its exposed interior surface a composition composed of a polymeric matrix with a substantially water insoluble oxygen scavenger and a substantially water-insoluble transition metal containing compound distributed therein. The oxygen scavenging composition comprises a carrier which contains (a) a non-polymeric oxygen scavenger and (b) a water-insoluble oxygen scavenging catalyst having higher affinity to organics than to water. More specifically, the catalyst is composed of a water-insoluble, compound of a transition metal. The present oxygen scavenging composition provides effective absorption of oxygen from the interior of a container without adversely affecting the color, taste or smell of the packaged material contained therein.

It is known in the art that ascorbate compounds (ascorbic acid, its salts, optical isomers, and derivatives thereof), as well as sulfite salts can be oxidized by molecular oxygen, and can thus serve as components of an oxygen scavenging formulation, for example, as a component of a closure compound. For example, U.S. Pat. No. 5,075,362, issued to Hofeldt et al., discloses the use of ascorbates in container closures as oxygen scavengers.

It is highly desired to provide an effective oxygen scavenging system suitable for packaging applications which has good oxygen absorption capabilities and which does not leach out of the system to adversely effect the color, taste or smell of the packaged material.

It is further desired to provide an improved container which incorporates the subject oxygen scavenging composition as a part of the interior of the container to provide effective oxygen scavenging without adversely effecting the color, taste or smell of the packaged material.

The present invention is directed to an oxygen scavenging composition capable of providing good oxygen absorption capabilities while not adversely affecting the color, taste or smell of material packaged within a container having said composition as a part thereof. The present oxygen scavenging composition is composed of a polymeric matrix having an ascorbate compound and a substantially water-insoluble, organic compound of a transition metal distributed within the matrix.

In one aspect of the present invention there is provided an oxygen scavenging composition comprising at least one non-polymeric oxygen scavenging material and at least one substantially water-insoluble transition metal compound effective to catalyze the reaction of oxygen with the oxygen scavenging material. In a preferred embodiment of the present invention, the oxygen scavenging composition is composed of at least one water-insoluble oxygen scavenging material and at least one water-insoluble transition metal compound.

In another aspect of the present invention there is provided a polymeric composition comprising a polymer matrix having the above described oxygen scavenging composition incorporated therein.

In. particular, the polymeric material can be generally selected from polyolefins as, for example, polyethylene, polypropylene, ethylene/propylene copolymers, acid modified ethylene/propylene copolymers, polybutadiene, butyl rubber, styrene/butadiene rubber, carboxylated styrene/butadiene, polyisoprene, styrene/isoprene/styrene block copolymers, styrene/butadiene/styrene block copolymers, styrene/ethylene/ butylene/styrene block copolymers, ethylene/vinyl acetate copolymers, ethylene/acrylate and ethylene/ (meth) acrylate copolymers (for instance, ethylene/butyl acrylate or ethylene/butyl methacrylate copolymers), ethylene/vinyl alcohol copolymers, vinyl chloride homopolymers and copolymers, styrene/acrylic polymers, polyamides, and vinyl acetate polymers, and blends of one or more of these. Polyethylenes found useful in forming the subject composition include high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), ultra-low density polyethylene (ULDPE) and the like as well as copolymers formed from ethylene with one or more other lower alkenes (e.g., octene) and the like.

In this embodiment, particularly preferred compositions according to the invention are thermoplastic compositions formed of polyethylene or copolymers of polyethylene such as, for example, ethylene/vinyl acetate and the like or polyethylene blends such as, for example blends of HDPE and butyl rubber; polyethylene and ethylene/vinyl acetate copolymer; as well as polyethylene and styrene/butadiene/styrene block polymer and the like. The polyethylene, if used, is preferably a low density polyethylene, and may be a very low or ultra low density polyethylene which may be branched or linear. The ethylene/vinyl acetate copolymer, if used, preferably has a melt index in the range 3 to 15, preferably 5 to 10, and generally contains 5 to 40%, preferably 5 to-30%, vinyl acetate.

The oxygen scavenger agents found useful in providing an effective oxygen scavenging composition of the present invention are ascorbates and isoascorbates (as free acid, salts and derivatives), alkali metal, alkaline earth metal or ammonium sulfite salts or mixtures thereof. The most preferred oxygen scavenger agents are water insoluble ascorbates.

The subject oxygen scavenging composition is preferably formed using ascorbates or isoascorbate compounds or mixtures thereof. The ascorbates and isoascorbates are preferably introduced into the composition as an ionic metal salt such as alkali metal, or alkaline earth metal salt or as an ester of an organic acid (esterified at the 5 or 6 position hydroxyl group of ascorbic acid) or other derivatized ascorbate [e.g., in which the 5 or 6 hydroxyl group is reacted with an organic compound to provide an unsubstituted or substituted (carbonyl, carboxyl, hydroxy,ether) branch group(s) therefrom]. The oxygen scavenger ascorbate and/or isoascorbate component may be supplemented with other known reducing agents as, for example, a second ascorbate or isoascorbate, tannin, sulfite and the like. It is preferred that

the ascorbate and/or isoascorbate be the sole oxygen scavenger or at least be the major scavenger agent of a mixture of oxygen scavengers. The term "ascorbate" shall refer herein and in the appended claims unless specifically stated otherwise, to ascorbic acid and isoascorbic acid as the free acid, their salts, their ester derivatives and other derivatives which provide ascorbate capable of reacting with oxygen under redox conditions.

The oxygen scavenging composition can be formed using sulfite salts of an alkali metal, an alkaline earth metal, transition metal or ammonium cation or mixtures of said salts. The sulfites can be used as the sole oxygen scavenging agent or, preferably, can be used in combination with at least one ascorbate. When mixtures are used, it is preferred that the ascorbate be the major scavenging agent of the present composition.

In a preferred embodiment the oxygen scavenging agent can be selected from water-insoluble ascorbate compounds, water-insoluble sulfite salts and mixtures thereof. Water-insoluble sulfites are, for example, alkaline earth metal and transition metal sulfites. Water-insoluble ascorbates are described herein below. The scavenging agent may have any degree of water-insolubility. The lower the water solubility the more preferred the agent. For example, the agent can have water solubility of less than 10 gm per 100 cc water, preferably less than 4 gram, more preferably less than 1 gm and most preferably less than 0.1 gm per 100 cc water at 25.degree. C.

The most preferred oxygen scavenging agents of the present composition are selected from ascorbate compounds which have limited or no water solubility. The ascorbates and isoascorbates are preferably introduced into the composition as an alkaline earth metal salt or as an ester of a fatty acid or other organic derivative (derivatized at either the 5 or 6 or both position hydroxyl group of ascorbic acid). The oxygen scavenger ascorbate component may be supplemented with other known reducing agents as, for example, a second ascorbate or isoascorbate, tannin, a sulfite salt, and the like.

The subject ascorbates are preferably introduced into the above-described polymeric matrix in the form of a substantially water-insoluble salt, as for example, an alkaline earth metal salt, such as calcium ascorbate, barium ascorbate and the like. The ascorbate may also be in the form of a C.sub.6 -C.sub.22 fatty acid ester or diester which may be fully saturated or contain unsaturation in the hydrocarbon chain with a C.sub.10 -C.sub.22 fatty acid ester being preferred. The ascorbate ester may be, for example, ascorbyl laurate, ascorbyl myristate, ascorbyl palmitate, ascorbyl stearate and the like. The saturated acid esters are preferred and most preferred is ascorbyl palmitate.

A third component of the present composition is an oxidation catalyst which has limited or no water solubility.

It has been unexpectedly found that one can provide an effective oxygen scavenging composition by utilizing an organic or inorganic transition metal compound which is substantially water insoluble; that is, it is highly hydrophobic and, when the carrier is a polymer matrix, has a high affinity to the organic polymer matrix of the composition. The water-insoluble inorganic transition metal compound may be in the form of a salt or compound in which the transition metal is associated with other elements or groups by ionic or covalent bonds.

The water-insoluble organic transition metal compound may be in the form of a chelant, complex or organic carboxylic acid salt. The water insolubility of the catalyst should be less than 4 grams, preferably less than 2 grams, still more preferably less than 1 gram, and most preferably less than 0.1 gram per 100 cc of water at 25.degree. C. Substantially complete water insolubility is highly desired.

It is preferred that the transition metal compound be a compound having the transition metal in its highest oxidation state. The term "compound" as used as used in the context of transition metal oxidation state refers to materials which preferably has the transition metal in its higher active valence state and is bound to a counter moiety as in a salt, complex or other form to provide a stable material. The transition metals are the series of metals in the Periodic Table from scandium to zinc (i.e., Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn). The preferred compounds are those of copper and iron with copper compounds being most preferred. Even though these catalysts have a low propensity to migrate from the carrier, and in particular the polymeric matrix in which they are contained, into the aqueous phase where the oxidation is deemed to occur, it has been unexpectedly found that the present oxygen scavenging composition gives comparable or better performance than typical systems using water soluble catalysts.

Other transition metal compounds providing usable catalysts include transition metal-ion-loaded zeolites. It is known that metal loaded zeolites, wherein the metal is in the zero oxidation state, can function as primary oxygen scavengers and that at least some of the same metals do not appreciably scavenge oxygen in other oxidation states. It has been found, however, that the metal ion-loaded zeolite with the metal in the higher valence state can be used to catalyze oxygen scavenging activity of another primary oxygen scavenger.

The preferred transition metal compounds are metal salts of mono- and di-carboxylic acids having a carbon chain length of C.sub.2 -C.sub.20 or so. The carbon chain can be aliphatic or aromatic, substituted or unsubstituted, and may contain unsaturation, and may be fatty acids. These salts have low to no solubility in water at ambient temperature. Examples of aliphatic monocarboxylic acids include acetic, propionic, butyric, valeric, lauric, tridecanoic, myristic, pentadecanoic, palmitic, stearic, nonadecanoic acids and the like; of aliphatic dicarboxylic acids include malonic, succinic, glutaric, adipic, pimelic, azelaic, sebacic acids and the like; acids having unsaturation include hydrosorbic, sorbic, butyric, glutaconic, hydromuconic, octenedioic acid and the like; and aromatic acids including benzoic acid and the like. The acid may be substituted with hydrocarbyl groups which may be straight or branched chains, typically aliphatic having 1 to 5 carbon atoms or aromatic groups. The acids may have other substitution groups which do not effect the contemplated material to be contained in the resultant package container as is well known by those skilled in the art. The term "fatty acid", when used, is employed for convenience, and it is not intended to signify that it must be derived from natural sources, since it may be manufactured synthetically. The term refers to higher carbon monoacids, preferably having the carboxyl group located terminally. The term "hydrocarbyl" is used herein to include substantially hydrocarbyl groups as well as purely hydrocarbyl groups. The description of these groups as being substantially hydrocarbyl means that they contain no non-hydrocarbyl substituents or non-carbon atoms which significantly affect the hydrocarbyl characteristics or properties of such groups relevant to their uses as described herein.

Thus, the subject oxygen scavenging composition requires a water-insoluble transition metal compound in conjunction with a scavenger agent selected from an ascorbate compound,

sulfite salt or mixtures thereof. It is preferred that the catalyst be an organic transition metal compound, as described hereinabove. Further, it is preferred that the scavenger agent be selected from substantially water-insoluble ascorbates or sulfites, as described above. Thus, the preferred combination of scavenger and catalyst is such that both the scavenger and catalyts are water insoluble and most preferred combination is formed from a water-insoluble ascorbate and an organic transition metal compound. The transition metals preferred are copper and iron with copper being most preferred. The agent and catalyst are in a carrier which is preferably a polymer matrix, as described above.

It has been unexpectedly found that the present oxygen scavenging composition gives comparable or better performance than typical systems using water soluble catalyst, even though these catalysts have a low propensity to migrate from the polymeric matrix in which they are contained into the aqueous phase where the oxidation is deemed to occur.

The oxygen scavenger agent may be present in a wide range of amounts depending on the specific application to which the subject composition is applied. Normally, it should be present in at least about 0.1 weight percent based on the polymer matrix of the composition. As exemplified below, amounts of from 0.1 to 90 weight percent, preferably from 1 to 60 and most preferably from 2-60 weight percent provide effective oxygen scavenging when in the present composition.

The amount of the scavenger is dependent on the type of application. When the scavenger is incorporated into a gasket, the amount is normally at least 0.1 weight percent based on the polymeric matrix material, generally at least 1% and preferably at least 2%. It is generally unnecessary for the amount to be above 20% and 4%-10% is often a convenient maximum. Expressed in an alternative manner, the amount of scavenger is typically in the range 0.001 to 2 grams, often 0.02 to 0.1 grams, per container.

When the composition is in the form of a film, coating, mat, pouch or sachet, the oxygen scavenger should be present in an amount to effectively scavenge oxygen during the contemplated storage period of the container for the appropriate contents. The amount is normally in the range of from 0.01 to 2 grams per container of normal size.

In the case of a plastisol, lacquer, or hotmelt applied to the center panel of a closure, where the matrix does not otherwise serve as a gasket, scavenger loadings can be much higher. For example, loadings of 20 weight percent to 60%, or in some cases up to 90%, are workable.

The catalysts described above should be present in the subject composition in mole ratio of ascorbate to transition metal of from about 3000:1 to 20:1 with from 2000:1 to 20:1 being preferred and from 1000:1 to 100:1 being most preferred. In certain applications the ratio may be greater or lesser to provide for effective scavenging of oxygen.

By the invention it is possible to greatly prolong the product quality or shelf life of an oxygen sensitive material in a sealed container by reducing the degree of oxygen degradation.

It is preferred that the scavenger agent remain substantially inert in the subject composition until it is contained within a sealed container. As mentioned above, the composition as whole is preferably anhydrous and the polymeric matrix is also preferably anhydrous. Therefore, the polymeric matrix substantially protects the scavenger agent from moisture under normal atmospheric conditions. Exposure of the composition to the high humidity that normally

exists within a sealed container results in sufficient permeation of moisture into the composition as part of the container to initiate a satisfactory degree of scavenging and result in improved shelf life of the packaged material. However, the scavenging reaction can be further accelerated by heating the composition in the closed container to cause increased permeation of moisture. Thus, preferably the scavenger is a material that remains substantially inert in the carrier until the scavenging reaction is accelerated by heating in the presence of moisture.

For example, the scavenging reaction of the present composition is accelerated by pasteurizing (typically at 50.degree. to 100.degree. C.) or sterilizing (typically at 100.degree. to 150.degree. C.) the container after filling it with an aqueous-based fill and sealing it, using the composition of the invention. This triggering appears to be a consequence of the composition, when heated, permitting moisture to permeate into the composition and to become trapped in the composition thereby bringing the scavenger into contact with sufficient water to permit reaction with oxygen. This oxygen may permeate through the composition either from oxygen trapped within the container when it was filled or which subsequently enters the container from the surrounding atmosphere.

It may be desirable to include in that composition a material, for instance a surfactant such as sodium dodecylbenzene sulfonate, which will increase the permeability of the composition to water and a suitable amount of a surfactant such as this is between 0.1 and 1.0% by weight.

In preferred embodiments, the concentrate is diluted in a ratio of between about 1:38 and 1:1, and more preferably between about 1:13 and 1:1 concentrate to base resin. In these concentrate formulations, it is preferred to use an amount of oxygen scavenging compound ranging from about 10 to 50% by weight and more preferably from about 20 to 40% by weight (i.e., between about 500 and 2500, and preferably between 1000 and 2000 micromoles of scavenger compound per gram of polymer for compounds having molecular weights of between 200 and 500 grams per mole). When an ascorbate is used as the scavenger, the catalysing agent of the transition metal element compound or complex may be used in an amount of about 0.3 to 8% by weight (i.e., between 40 and 200 micromoles per gram of polymer). More preferably, the catalysing agent is used in an amount of about 0.6 to 2% by weight.